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Testing and Evaluation of On-Farm Alcohol Production Facilities

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TESTING AND EVALUATION OF ON-FARM ALCOHOL PRODUCTION FACILITIES

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16. ABSTRACT

Ethanol is the most important of biomass derived fuels in the short term. The bulk of the production will come from large (20 to 600M gallons/year) units with the remainder being produced on-farm in small (less than 6,000 gallons/year) units. The on-farm production of alcohol presents a unique problem in that the Environmental Protection Agency (EPA) had no data available by which it could evaluate the possible impacts of a very large number of these facilities. This report gives the results of a sampling and analysis program conducted to characterize the air emissions, water effluents, and solid residuals from two on-farm ethanol production processes sampled in June 1980.

Several recommendations, including acid neutralization and effluent ponding, are recommended to minimize the impacts.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts of our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

A multimedia environmental study of farm production of alcohol fuels has been made. This study was conducted to acquire basic information about the amount and type of pollutants present in the on-farm ethanol production process. The information can be used to determine the environmental impacts from small-scale ethanol production units. It should prove useful as a guide to individuals planning to produce alcohol or are currently doing so.

Alcohol fuels are expected to make significant contributions to reduction of U.S. oil imports in the future. Further information on alcohol fuels can be obtained from the IERL-Cincinnati Incineration Research Group.

David G. Stephan
Director
Industrial Environmental Reserch Laboratory

ABSTRACT

Alcohol fuels are expected to contribute significantly to the reduction of oil imports in the near future, with ethanol being the most important in the short term. There are two facets to the ethanol production picture. The bulk of the production will come from large (20 to 600M gallons/year) units with the remainder being produced on-farm in small (less than 6,000 gallons/year) units. The on-farm production of alcohol presents a unique problem in that the Environmental Protection Agency (EPA), because of the small unit size, has no direct means to regulate discharges from on-farm units. Also no data are available by which EPA could evaluate the possible impacts of a very large number of these facilities. This report gives the results of a sampling and analysis program conducted by Acurex to characterize the air emissions, water effluents, and solid residuals from two on-farm ethanol production processes sampled in June 1980.

Gaseous emissions, both vented and ambient, were analyzed in the field for CO_2, O_2, and hydrocarbons including some 21 alcohols and aldehydes. No significant air emission problems were identified.

Liquid and solid samples of the feedstock, make-up water, distillation feed, byproduct, beer bottoms, product, and washout water were analyzed in the laboratory for priority pollutants, metals, herbicides and pesticides, and other standard chemical analysis (e.g., Biological Oxygen Demand, Chemical Oxygen Demand). The most significant result was the identification of very high Biological Oxygen Demand, Chemical Oxygen Demand, Total Organic Carbon, and Total Suspended Solids levels in both process and waste streams. The streams were also acidic (i.e., pH less than 4). The levels of priority pollutants were below current promulgated Resource Conservation and Recovery Act standards, but some metals exceeded selected state standards.

Several recommendations, including acid neutralization and effluent ponding, are recommended to minimize the impacts.

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SECTION 1

INTRODUCTION

Alcohol fuels will contribute significantly to the reduction of oil imports in the near future. In his speech of January 11, 1980, President Carter outlined an ambitious program designed to stimulate alcohol production for fuel use. The technologies exist for mass production of a suitable fuel, the major roadblock being a lack of production capacity. With the proper backing and incentives, such as those being discussed by the Administration and Congress, production capacity will rise sharply. The Administration predicts that the production rate of alcohol in 1981 will reach 500,000 gallons/year.

There are two facets to the ethanol production picture. The bulk of the production will come from large (20 to 600M gallons/year) units. The remainder will be produced on-farm in small (less than 6,000 gallons/year) units. The environmental effects of a vast industrial alcohol industry are currently under study. A program to study several plants currently producing alcohol is underway; this will result in regulations for the industry.

On the other hand, the on-farm production of alcohol presents a different problem. The Environmental Protection Agency (EPA), because of the small unit size, has no direct means to regulate discharges from on-farm units. No data is available by which EPA could evaluate the possible impacts of a very large number of these facilities. This report gives the results of a sampling and analysis program conducted by Acurex to characterize the air emissions, water effluents, and solid residuals from on-farm ethanol production processes.

The objective of this program was to test and characterize the emission from two farm-scale (approximately 6,000 gallons/year) ethanol production facilities. The Energy & Environmental Division of Acurex Corporation, under Contract 68-03-2567 to EPA, visited eight farm-scale ethanol production facilities in Kansas, Missouri, and Nebraska. The visits were conducted in April and May of 1980 and had the following purposes:

- To determine if each facility was suitable for environmental sampling
- To determine if each facility could be sampled within the time period allotted for this program

- To meet with the owners of each facility and determine if they were genuinely interested in participating in the test program

Based on these visits, two of the facilities met these criteria, and were sampled in June 1980. Section 2 of this report describes the processes at the two facilities, Section 3 presents the techniques used to acquire the samples for analyses, Section 4 outlines the analytical techniques used, and Section 5 presents the results and discusses the implications of the results and the environmental impact of these small-scale production facilities.

SECTION 2

PROCESS DESCRIPTION

The following discussion describes the two on-farm facilities tested during the program. Section 2.1 discusses the Kansas facility (Site A), while Section 2.2 discusses the Nebraska facility (Site B).

2.1 SITE A

Site A, shown in Figure 1, is located in central Kansas. The feedstock used in the process during the sampling period was corn. The corn was transported to the ethanol facility and ground on-site using a hammer mill.

Before adding the process make-up water, the cook tank was sterilized with steam to kill any bacteria present. At about 9:30 a.m. on June 10, approximately 900 gallons of make-up water (well water) at 54°F was pumped into the cook tank. This water was heated to 100°F by introducing live steam. Then at about 10:30 a.m., 75 bushels of ground corn were added to the cook tank by the corn hopper and conveyor shown in Figure 2. The corn displaced about 450 gallons of volume in the cook tank. The slurry was then heated with live steam to 130°F while being agitated. After reaching this temperature, 1 ounce/bushel of a carbohydrase enzyme (brand name Taka-Therm) was added. This enzyme is used to convert the corn starches to complex sugars called dextrins. After adding the Taka-Therm, the cook tank was heated to about 200°F with live steam and held at this temperature for about 45 minutes. During this time the tank was continually agitated. A starch conversion test (dripping iodine onto a slurry sample) was performed to verify starch conversion and then 300 gallons of make-up water was added to the tank to reduce the temperature to 170°F. An additional 300 gallons of make-up water was added reducing the slurry temperature to 138°F. After the temperature had stabilized, 1.5 ounces/bushel of a glucohydrolase enzyme (brandname Diazyme L-100) and 1 gallon of sulfuric acid were added. The enzyme causes the dextrins in the slurry to break down into simpler sugars called glucose. This process took about 6 hours. Throughout the conversion of starches to dextrins and then to glucoses, the cook tank was continually agitated. Once the conversion to glucose was complete, the slurry was cooled in a tube-in-shell heat exchanger (the cooling media being well water). When the cooker slurry had cooled to 89°F, it was transferred to the fermentation tank. This occurred at about 9:00 p.m. At this time the total volume of the slurry was about 2,150 gallons. Table 1 summarizes the make-up of the slurry. The cook tank was then flushed with washout water.

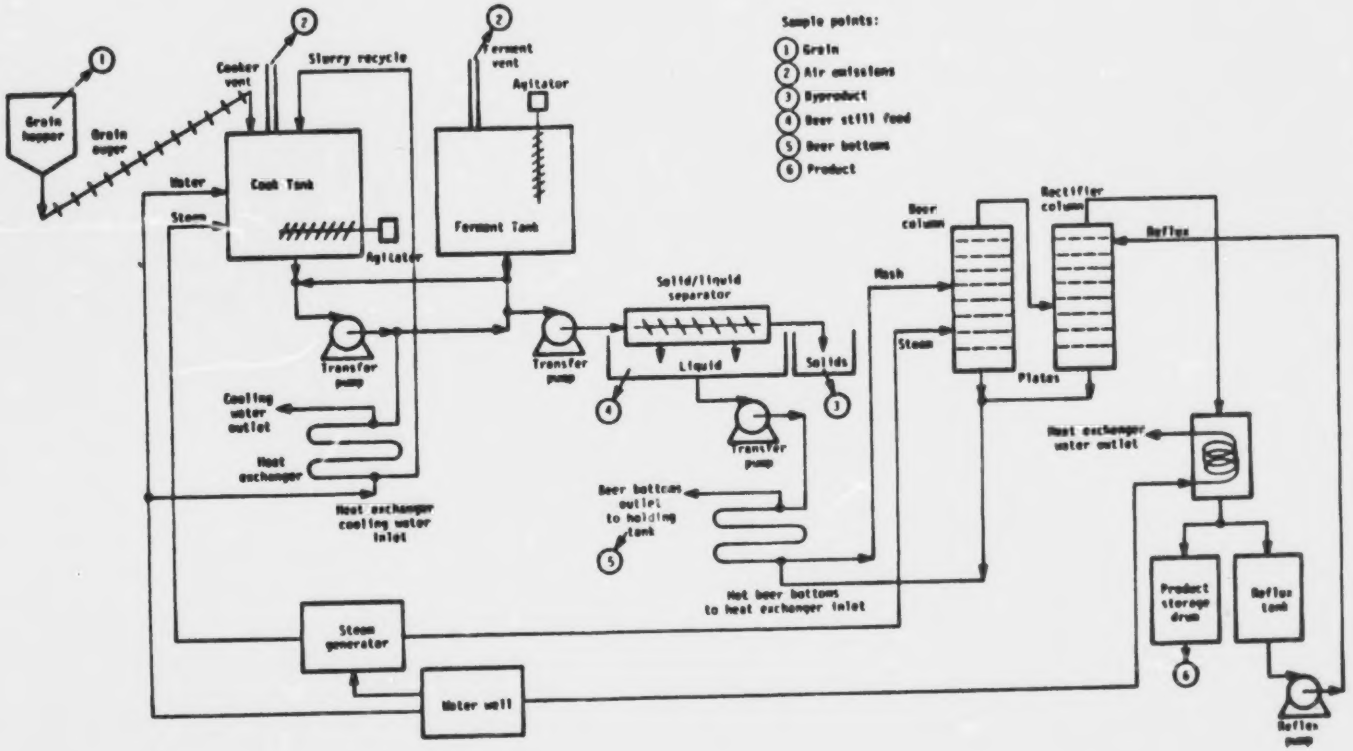
Sample points:
① Grain
② Air emissions
③ Byproduct
④ Beer still feed
⑤ Beer bottoms
⑥ Product
Grain hopper
Grain auger
Cooker vent
Slurry recycle
Water
Steam
Cook Tank
Agitator
Ferment vent
Agitator
Ferment Tank
Transfer pump
Cooling water outlet
Heat exchanger
Heat exchanger cooling water inlet
Transfer pump
Solid/liquid separator
Liquid
Solids
Transfer pump
Beer bottoms outlet to holding tank
Hot beer bottoms to heat exchanger inlet
Mash
Steam
Beer column
Rectifier column
Plates
Reflux
Heat exchanger water outlet
Product storage drum
Reflux tank
Reflux pump
Steam generator
Water well

Figure 1. Site A process diagram.

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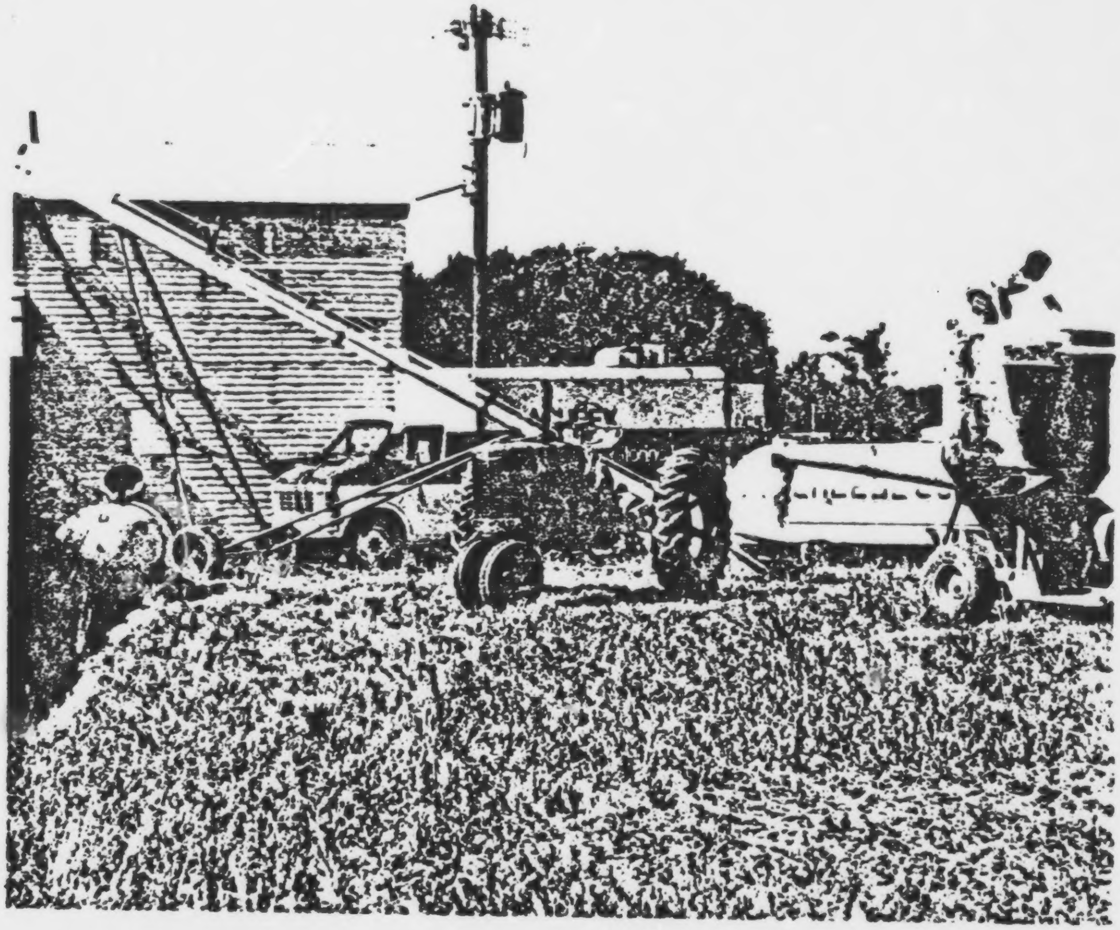

Figure 2. Corn hopper and conveyor.

TABLE 1. SITE A COOK TANK MAKE-UP

Item	Volume	Time	Temperature
Sterilize cook tank	--	--	212°F
Make-up water	900 gallons	9:30 a.m.	54°F
Steam	*	9:30-10:15	100°F
Corn	75 bushels (450 gallons)	10:30	--
Steam	*	10:30	130°F
Taka-Therm	75 ounces	11:30 p.m.	130°F
Steam	*	11:30	200°F
Make-up water	300 gallons	1:45	170°F
Make-up water	300 gallons	2:00	138°F
Diazyme L-100	110 ounces	2:00	138°F
Cooling	--	--	138°-89°F
Transfer to ferment tank	--	9:00 p.m.	89°F
*Total steam volume	200 gallons	--	--
Total	2,150 gallons		

Once the slurry was pumped into the fermenting tank, the yeast culture was added. The yeast culture was prestarted before addition into the fermenting tank by rehydrating 1 pound of yeast in 10 gallons of sugar water. The initial temperature of the distillation feed was 89°F. The sugar content of the mash was about 16.5° Brix. During the first 16 hours of fermenting, the slurry temperature increased as follows:

9:00 p.m. (6/10) → 89°F
9:00 a.m. (6/11) → 102°F
11:00 a.m. (6/11) → 105°F
1:00 p.m. (6/11) → 107°F

Once the temperature had reached 107°F, it became apparent that the mash had to be cooled. Since the alcohol plant operators had not experienced this rapid rise on other batches of mash, the heat exchanger had not been plumbed into the ferment tank. Therefore, the mash had to be transferred to the cook tank and then into the heat exchanger. The entire cooling process lasted from about 1:00 p.m. until 6:00 p.m. The time lapse was due to the piping and transfer equipment configurations that had to be made and because of a pump malfunction. After cooling, the temperature of the slurry was about 90°F. During this cooling cycle the mash was agitated causing mixing with ambient air. The mixing may have slowed the conversion of sugar to alcohol, but was necessary as the yeast culture would have become inactive at the higher temperature. By 9:00 a.m. on June 12, the temperature had risen to 100°F with a sugar content of about 6° Brix. At about 8:00 a.m. on June 13, a hydrometer reading indicated that almost all of the sugar in the mash had been converted to alcohol.

At this time, the distillation feed was pumped into the solid/liquid separator ("squeezer"). The squeezer consisted of a motor-driven auger, a filtering screen, a solids release plate, and a trough to collect the liquid. The squeezer is shown in Figure 3 with the fermenting tank in the background. The solids portion from the squeezer dropped on the floor and was later shoveled into a bin and used for livestock feed. The pile of solids is shown being sampled in Figure 4. After the ferment tank had been pumped out, it was washed out.

Once the squeezer trough had accumulated some liquid, the beer still was brought up to temperature with steam. Then the liquid was pumped from the trough into the beer still. Steam was added to the bottom of the beer still to vaporize the alcohol and maintain a temperature of 190° to 200°F at the column top. The beer bottoms or ethanol-stripped liquid from the beer still was pumped from the column through a shell-in-tube heat exchanger to preheat the beer still feed. It was then stored in a tank truck for transport to the fields where it was spread on the ground.

After some of the beer bottoms had been put into the tank truck it was determined, by taking an air sample above the liquid in the tank truck, that there was still some ethanol left in the beer bottoms. So, this liquid was repumped through the distilling system and further stripped of alcohol. It should be noted that this additional distillation may not have been

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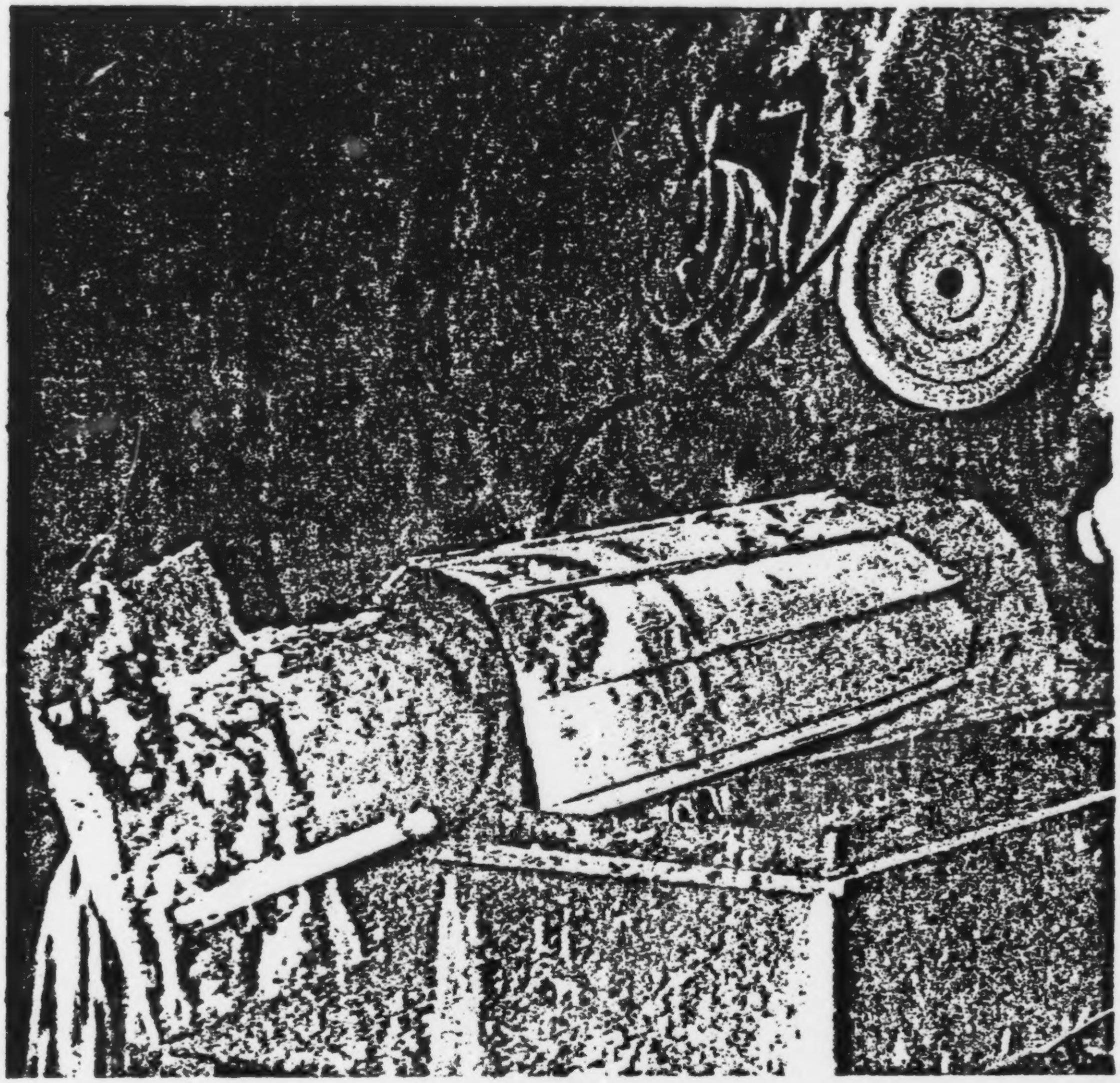

Figure 3. Solid/liquid separator ("squeezer") with ferment tank in background.

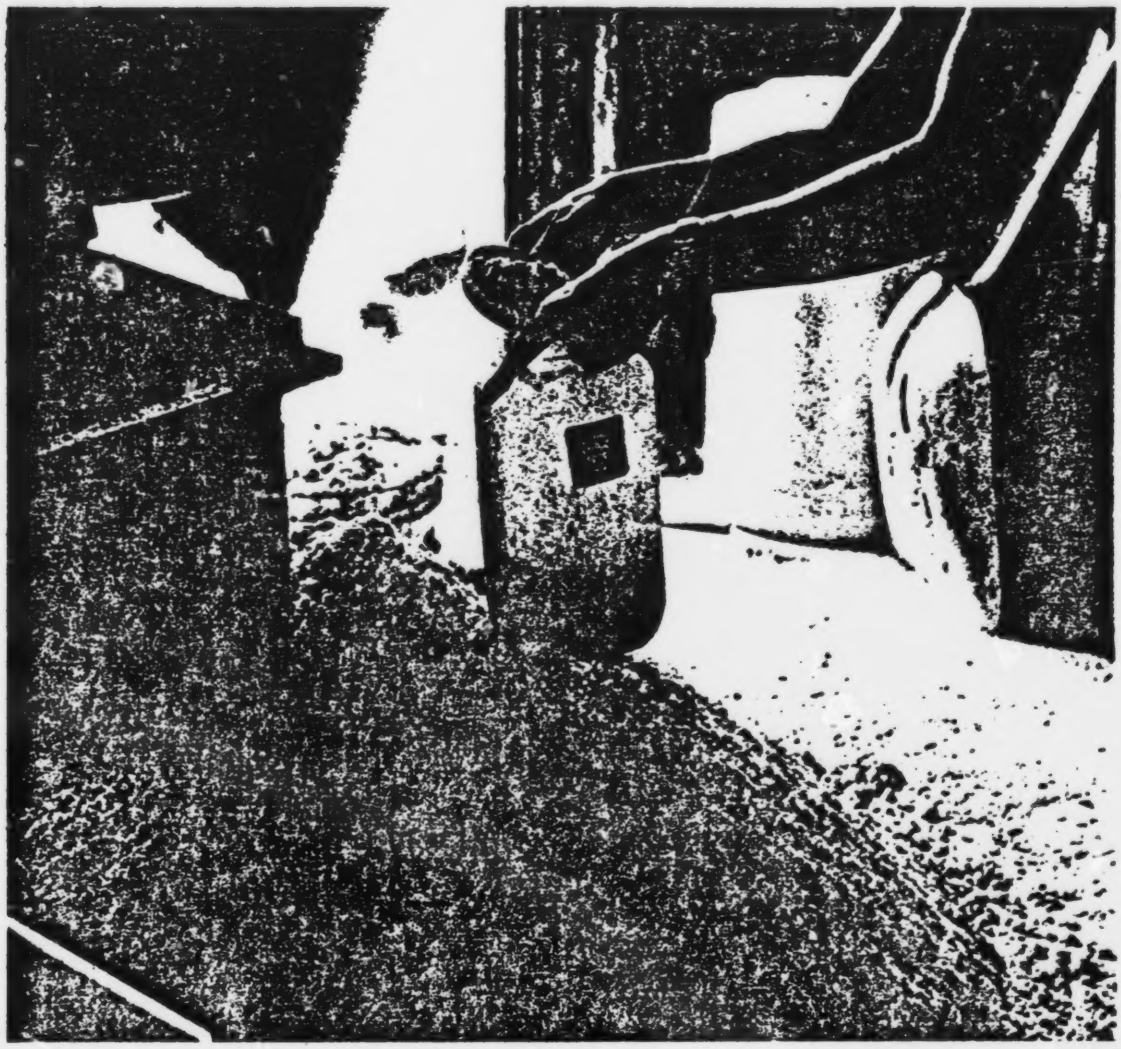

Figure 4. Squeezer solids sampling.

cost-effective due to the amount of energy used to recover a small amount of alcohol.

After passing through the beer still, the uncondensed vapors from the still went into a rectifier column. The temperature at the top of the rectifier column was controlled at 170°F by reflux (i.e., by pumping a portion of condensed product back into the column top). The temperature at the top of the column was shown on a temperature gauge.

The vapors from the rectifier were condensed in a water-cooled condenser. The product from the condenser flowed either into the reflux tank or into a product storage tank (55-gallon drums). Figure 5 shows the beer still, rectifier column, and reflux tank.

The squeezer, beer still, and rectifier were all washed out with water after the distillation was complete. All of the washings from the plant were discharged onto the ground outside of the plant.

All of the water used in the process (make-up, cooling, washout, and steam) was from a common well.

During the batch sampled, the process produced 126 gallons of 88.6 percent (177 proof) ethanol from the 75 bushels of ground grain (56 pounds per bushel) or a yield of 1.5 gallons of anhydrous ethanol per bushel of ground grain. Also produced were 10,400 pounds of byproduct for animal feed and 950 gallons of beer bottoms as waste. These two quantities were not measured directly but computed from a mass balance based on measured quantities and composition analysis. See Section 5 for detailed analysis of these effluents.

2.2 SITE B

Site B, shown in Figure 6, is located in central Nebraska. During the batch sampled, the process feedstock was corn. The corn was ground at a cooperative grinding facility and then transported to the ethanol production facility.

At 6:10 a.m. on June 17, 1980, the cook/ferment tank, pictured in Figure 7, was filled with about 155 gallons of make-up water at 140°F. The tan was not sterilized first. One pint of a carbohydrase enzyme (Taka-Therm) as added at about 6:45 a.m. By 7:30 a.m., 15 bushels of ground corn had been added to the tank. The corn increased the volume of the tank by about 100 gallons. The slurry temperature was now 115°F. Steam from the diesel-fuel-powered steam generator, pictured in Figure 8, heated the slurry to about 209°F by 8:25 a.m. The volume of the tank was now about 360 gallons and the slurry had a pH of 6.2 pH units. Approximately 3.5 gallons of diesel fuel was used to heat the slurry. The slurry was next cooled to 198°F by adding 35 gallons of make-up water at 9:00 a.m.

A second pint of Taka-Therm was added. By 10:40 a.m. the tank temperature was 190°F. At 11:00 a.m., 75 gallons of make-up water were

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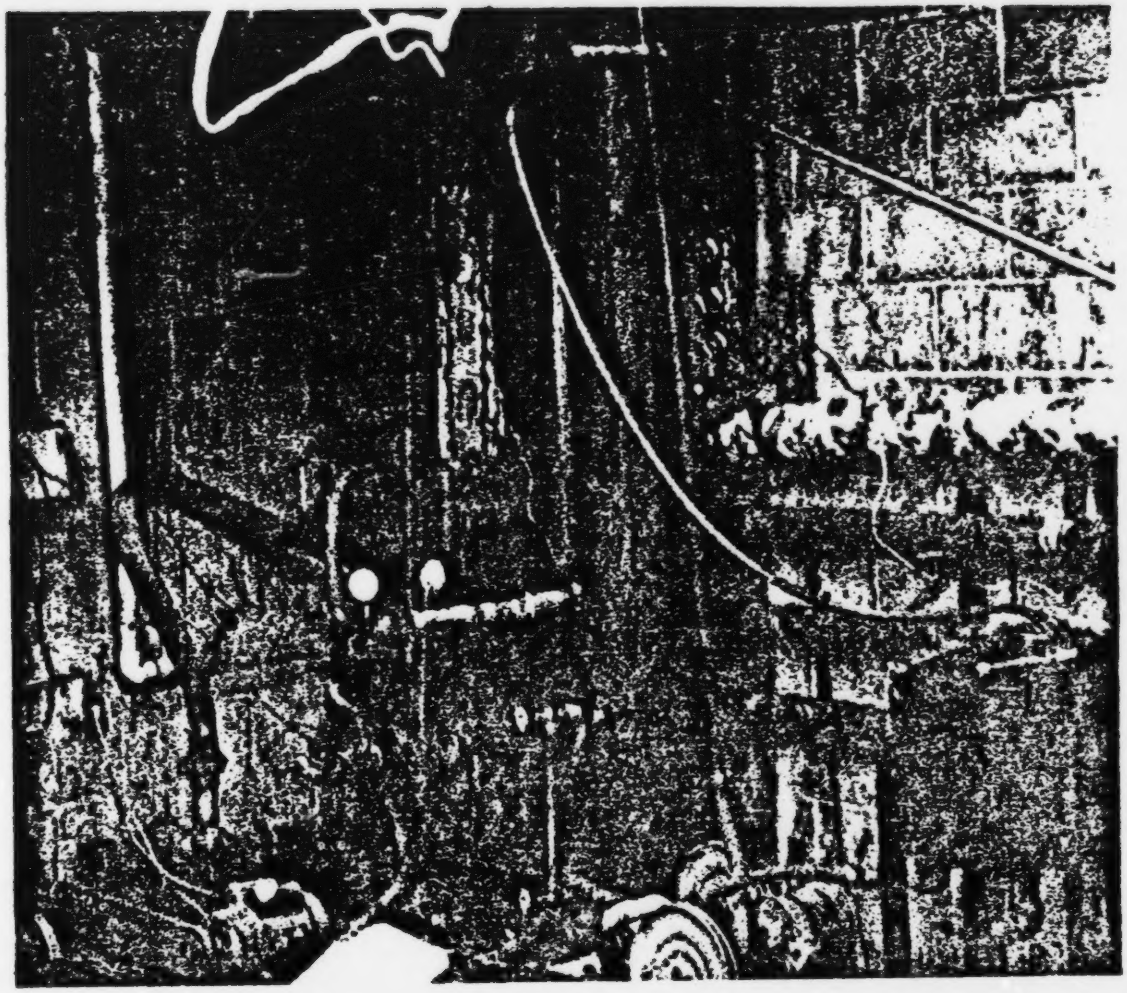

Figure 5. Beer still (left), rectifier column (right), and reflux tank (lower right).

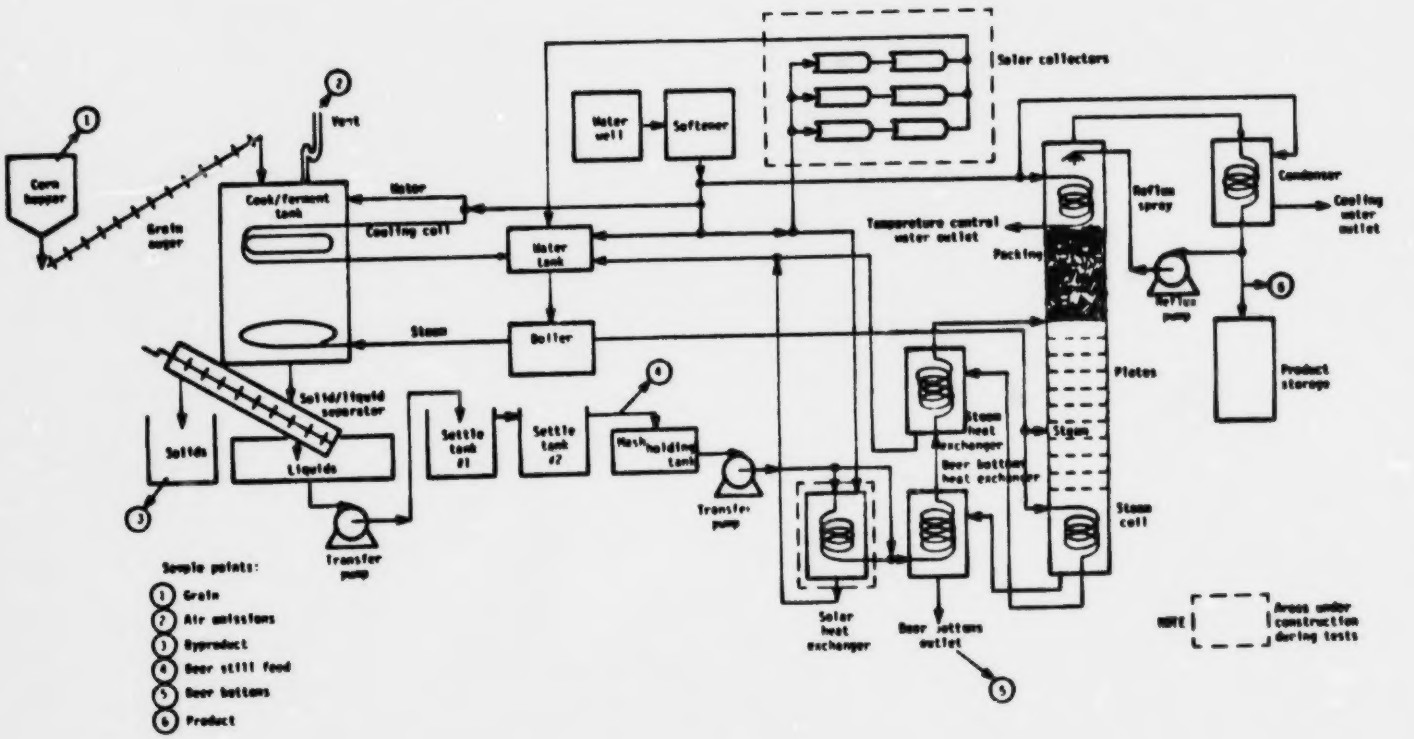
Corn hopper
Grain auger
Vent
Cook/ferment tank
Water
Cooling coil
Steam
Solid/liquid separator
Solids
Liquids
Transfer pump
Settle tank #1
Settle tank #2
Mash holding tank
Transfer pump
Water well
Softener
Water tank
Boiler
Solar collectors
Temperature control water outlet
Packing
Reflux spray
Condenser
Cooling water outlet
Reflux pump
Product storage
Plates
Steam heat exchanger
Steam
Beer bottoms heat exchanger
Steam coil
Solar heat exchanger
Beer bottoms outlet
NOTE
Areas under construction during tests
Sample points:
① Grain
② Air emissions
③ Byproduct
④ Beer still feed
⑤ Beer bottoms
⑥ Product
①
②
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Figure 6. Site B process diagram.

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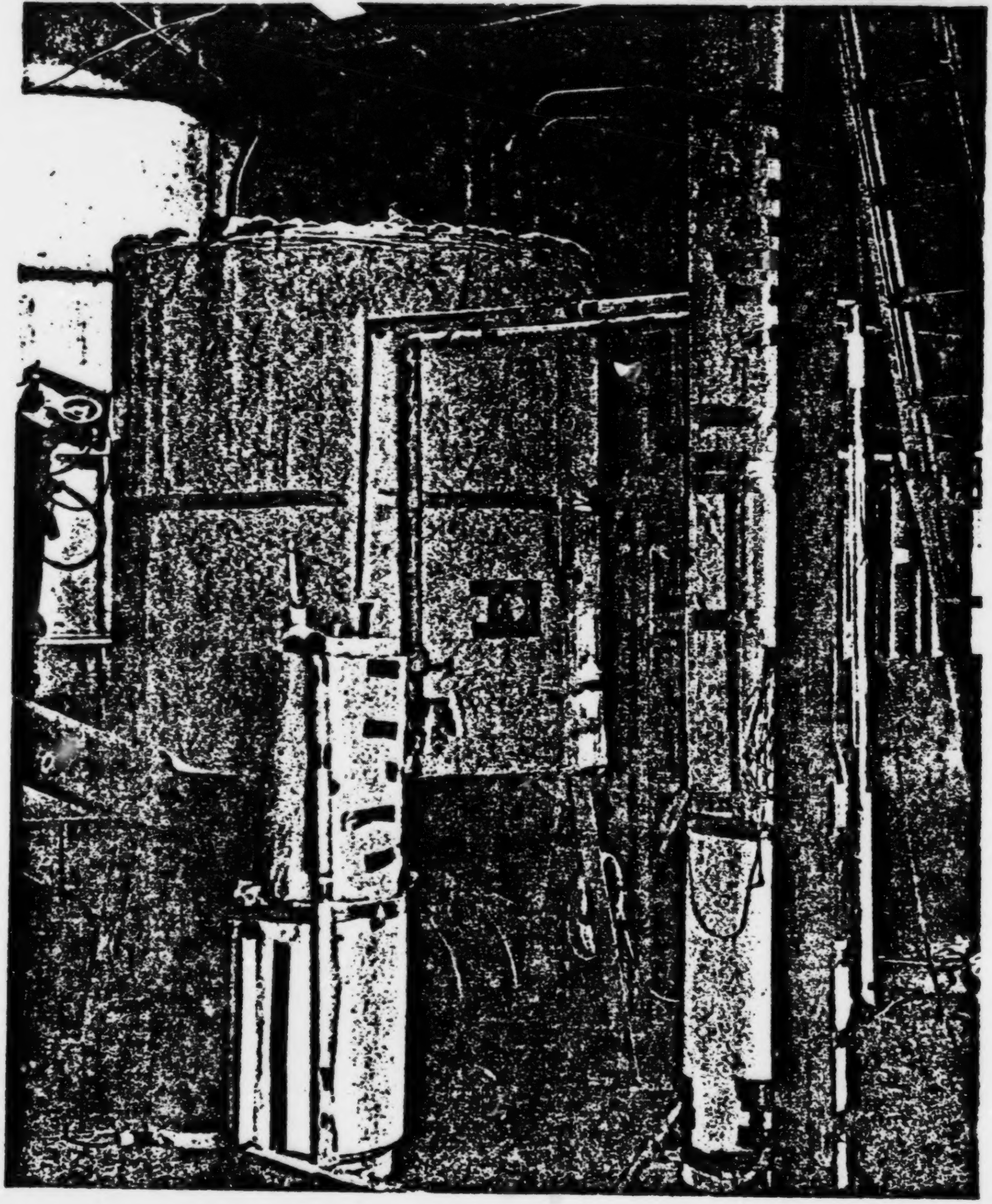

Figure 7. Cook/ferment tank with heat exchangers (foreground) and distillation column (right).

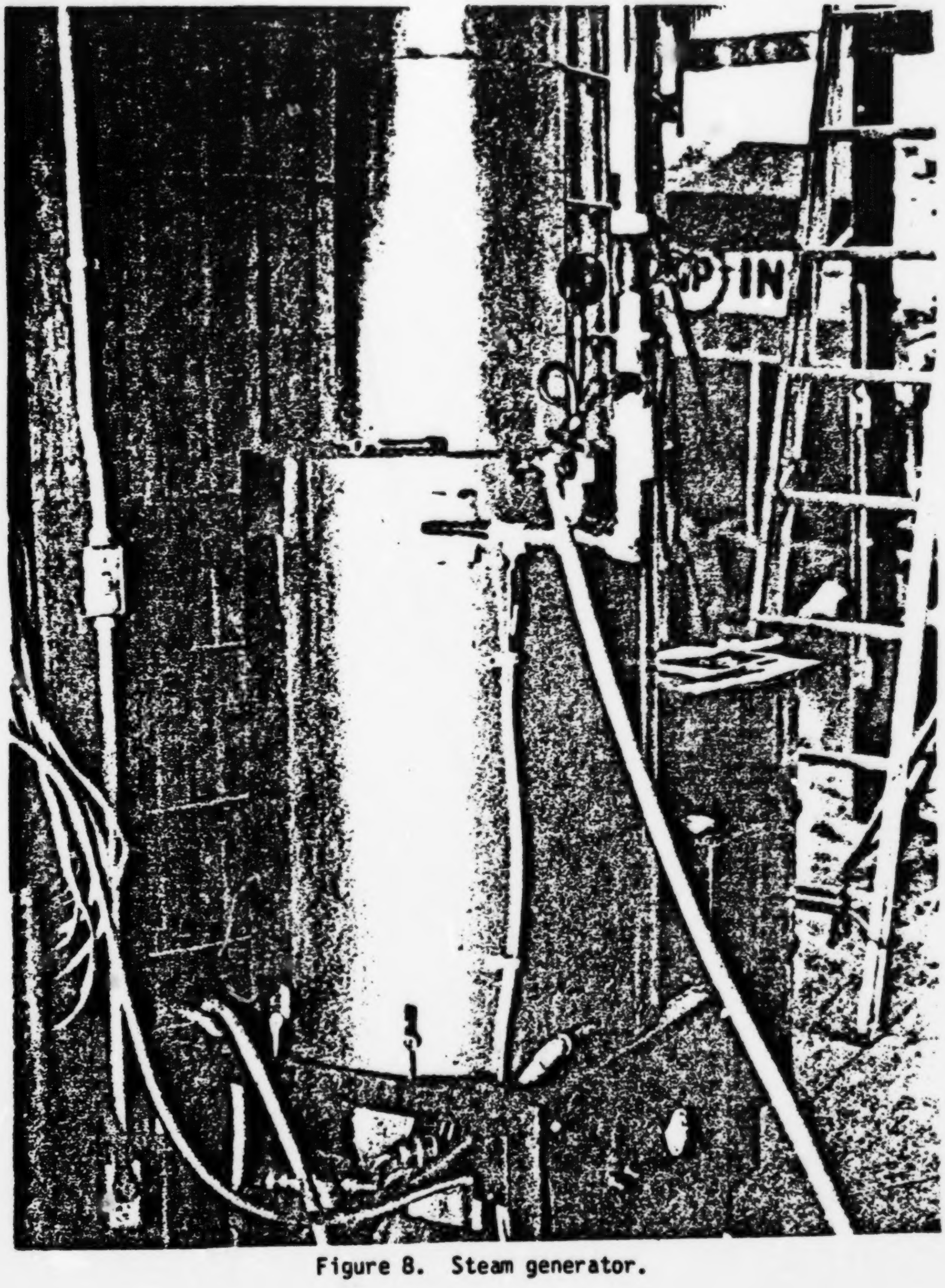

Figure 8. Steam generator.

added; the slurry volume was 470 gallons and the temperature was 170°F*. An additional 80 gallons of water were added reducing the temperature to 150°F* at 12:40 p.m. At 1:20 p.m., 1.4 pints of sulfuric acid were added to the slurry adjusting the pH to about 4.5 pH units. At 2:00 p.m., when the slurry temperature was 110°F (by mercury-in-glass thermometer), 2.5 pints of a glucohydrolase enzyme (Diazyme L-100) were added. At about 3:30 p.m., the cooling coil in the tank was activated. By 4:30 p.m. the temperature of the slurry was 91°F. The slurry was now ready for fermentation. Throughout the cooking process, the slurry was continually agitated.

Prior to adding the yeast and starting fermentation a sample of the cooker slurry was drawn and had the following characteristics:

pH	4.5 to 5.0
Temperature	84°F
Specific gravity	1.038
Potential alcohol	4.8 percent
Sugar content	9.5° Brix
Glucose	Approximately 5 percent

A listing of the make-up of the cook tank is shown in Table 2.

At about 4:15 p.m. the yeast was reactivated by adding 1 pound of the yeast to 1.5 gallons of the cooker slurry. The reactivated yeast was added to the balance of the slurry at about 4:50 p.m. The tank cover was then sealed (gases were vented) and allowed to ferment for 42 hours. The tank cover was opened a couple of times to accurately check the slurry's temperature. At about 8:00 a.m on June 17 the mash pH was about 5 pH units and the sugar content was about 0.1° Brix. Since fermentation was basically complete, the distillation equipment was readied.

The mash was removed through the bottom of the fermenter tank into a solid/liquid separator. As shown in Figure 6, solids are removed from the separator by a manually operated auger. The remaining solid/liquid mash was then pumped into a series of settling tanks where additional solid/liquid separation takes place. The solid/liquid separator, solids drum, and settling tanks are pictured in Figure 9. The solids, pictured in Figure 10, will eventually be used as animal feed.

After passing through the two settling tanks, the clarified liquor drains into a holding tank. From there, it is pumped through a series of heat exchangers. The first heat exchanger (not in service during this batch) will be heated by the solar collectors pictured in Figure 11 in the future. The second heat exchanger used the heat contained in the spent beer bottoms to preheat the clarified liquor. The third heat exchanger used the spent steam from the distilling column's steam coil. These heat exchangers are pictured in Figure 7.

---

*This temperature may be lower than indicated as the sheath on the bimetallic thermometer was found to be crushed during operation. See discussion on Table 2.

TABLE 2. SITE B COOK TANK MAKE-UP

Item	Volume	Time	Temperature
Make-up water	155 gallons	6:10 a.m.	140°F
Taka-Therm	1 pint	6:45	140°F
Corn	15 bushels (100 gallons)	7:30	115°F
Steam at 3 psig	105 gallons	8:25	209°F
Cooling water	35 gallons	9:00	198°F
Taka-Therm	1 pint	9:00	198°F
Cooling water	75 gallons	11:40	153°F[a] (170°F)
Cooling water	80 gallons	12:40 p.m.	119°F[a] (150°F)
Sulfuric acid	1.4 pints	1:20	115°F[a] (150°F)
Diazyme L-100	2.5 pints	2:00	110°F[b]
--	--	4:50	84°F[b]
Total	550 gallons		

[a] At 2:00 p.m., the sheath on the bimetallic thermometer used to measure the batch temperature with a reading using a mercury-in-glass thermometer showed that the bimetallic thermometer indicated 35°F high at that time. The temperature shown was computed from an energy balance. The temperature in parentheses was that indicated on the bimetallic thermometer. Previous temperatures appear correct.

[b] By mercury-in-glass thermometer

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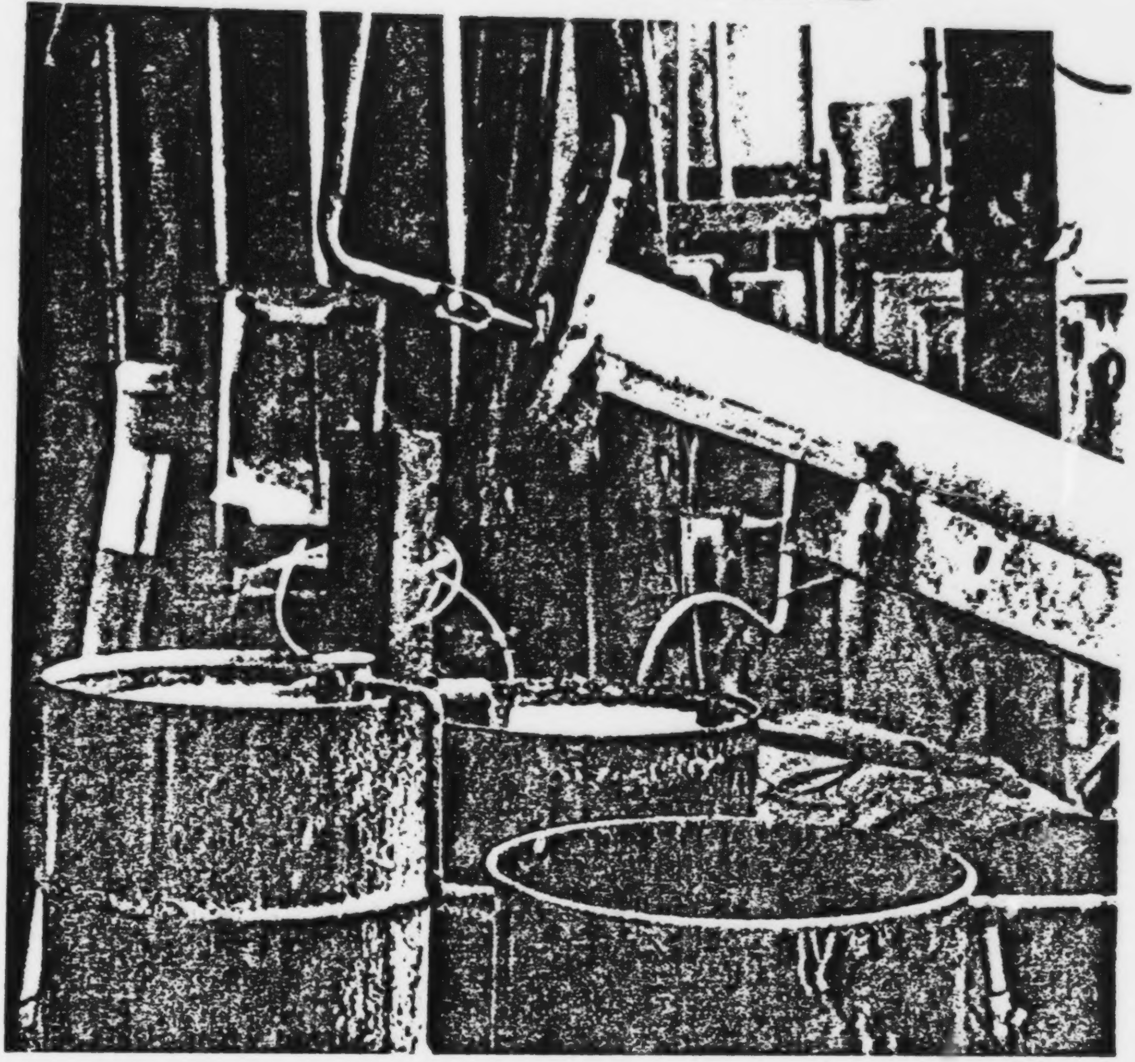

Figure 9. Solid/liquid separator, solids drum, and settling tanks.

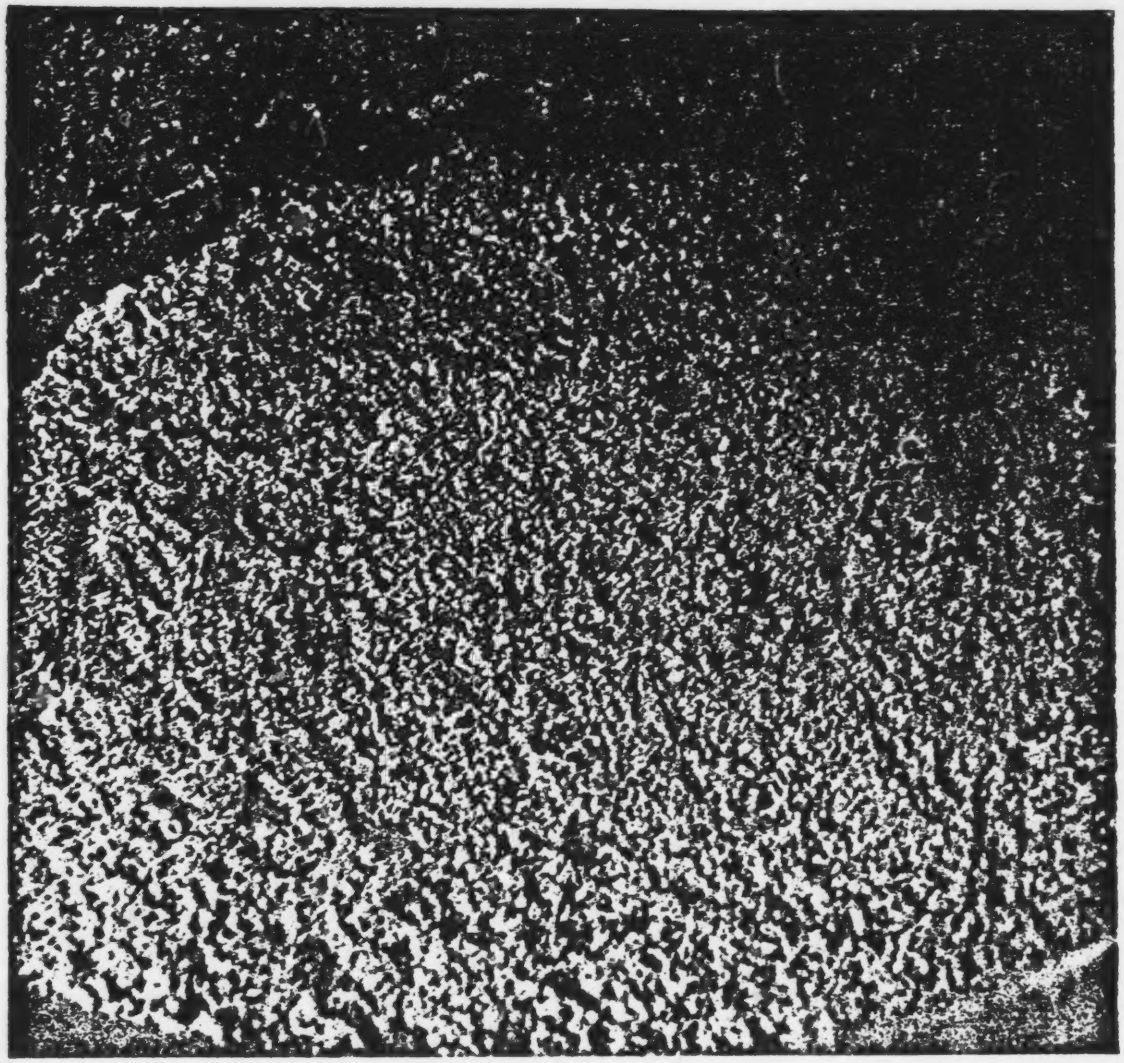

Figure 10. Solids from solid/liquid separator.

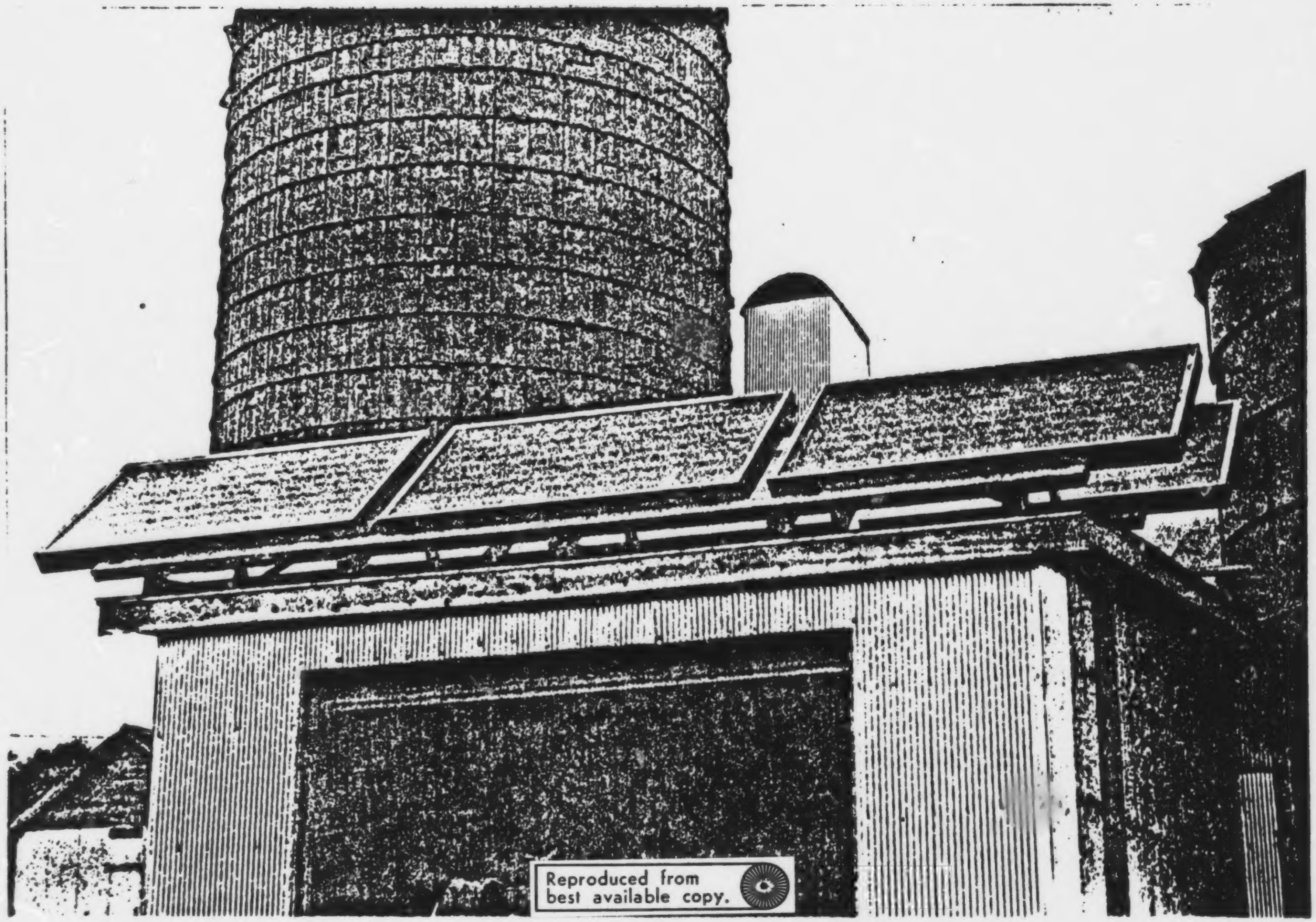

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Figure 11. Solar panels for steam generator water preheat and heat exchanger.

After being preheated in the heat exchangers, the clarified liquor is pumped into the distillation column. The column, pictured in Figures 7 and 12 measured 21 feet tall and 8 inches in diameter. The lower 12 feet of column contained 15 perforated plates, pictured in Figure 13, a steam coil, and a wet steam nozzle. The remaining 9 feet of column were filled with packing pictured in Figure 14, and also contained a cooling coil and reflux spray nozzle. During the tests, the cooling coil was rotated 90° from the position in the column cap shown in Figure 15 so that more of the coil's surface contacted the vapors.

The clarified liquor entered the column about 7 to 8 feet from the bottom of the column (i.e., in the upper portion of the perforated plate section). The vapor product was taken off the top of the column into the condenser shown in Figure 12. The previously mentioned cooling coil and the reflux spray (not working properly during this batch) are used to control the temperature of the top of the column at 170°F. After the alcohol vapors were cooled and condensed, the ethanol product went either to product storage or to the reflux.

After the distillation was complete, the entire system was washed out with water. This washwater, as well as the ethanol-stripped liquid from the beer bottoms heat exchanger was dumped onto the ground outside the barn. The dump site is shown in Figure 16.

During the batch sampled, the process produced about 13 gallons of approximately 73.6 percent (147 proof) ethanol from the 15 bushels of ground grain (56 pounds per bushel) or a yield of 0.6 gallon of anhydrous ethanol per bushel of grain. Also produced was 3,350 pounds of byproduct for animal feed and 145 gallons of beer bottoms as waste. These two quantities were not measured directly but computed from a mass balance based on measured quantities and composition analysis. See Section 5 for detailed analysis of these effluents.

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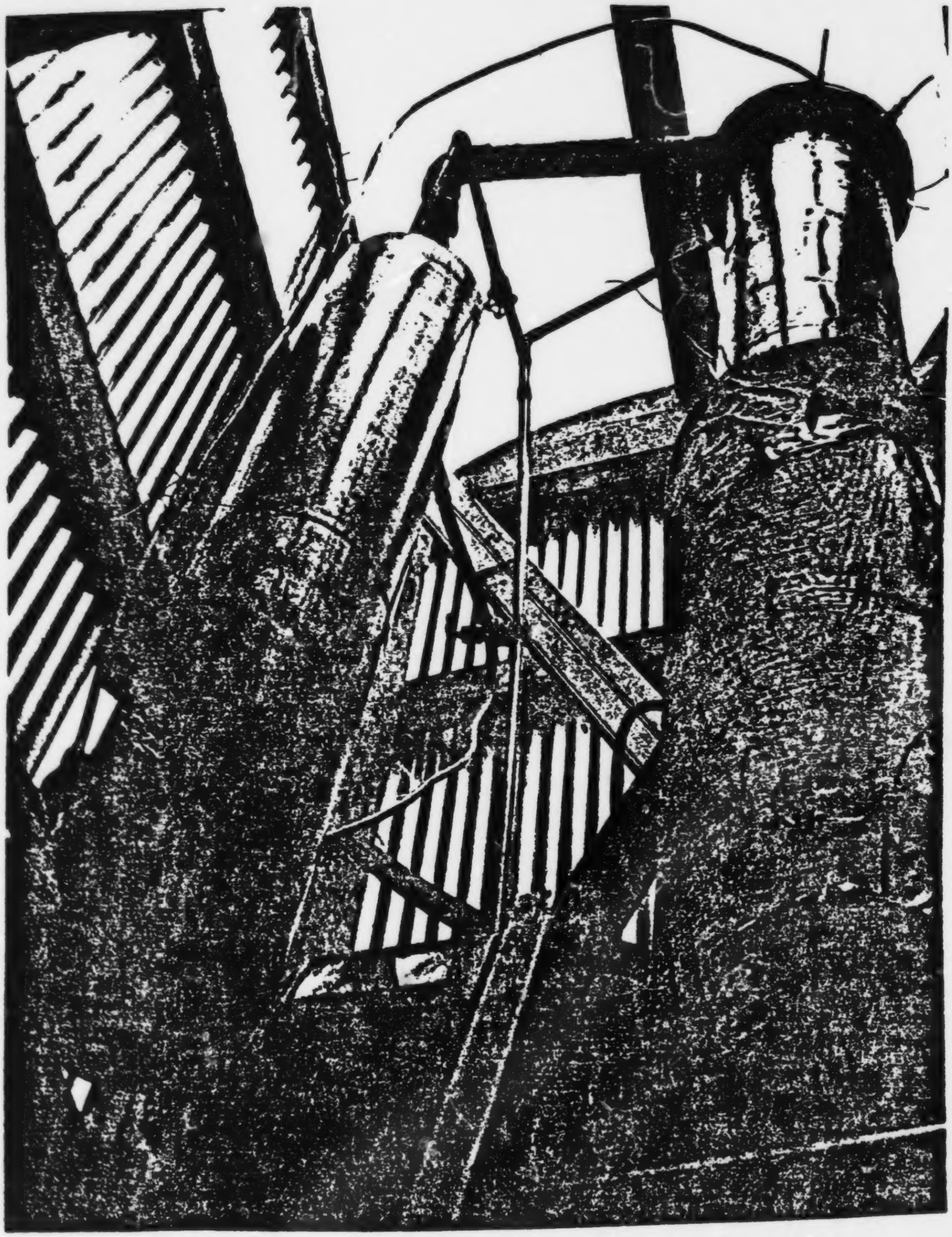

Figure 12. Top of distilling column (right) and condenser (left).

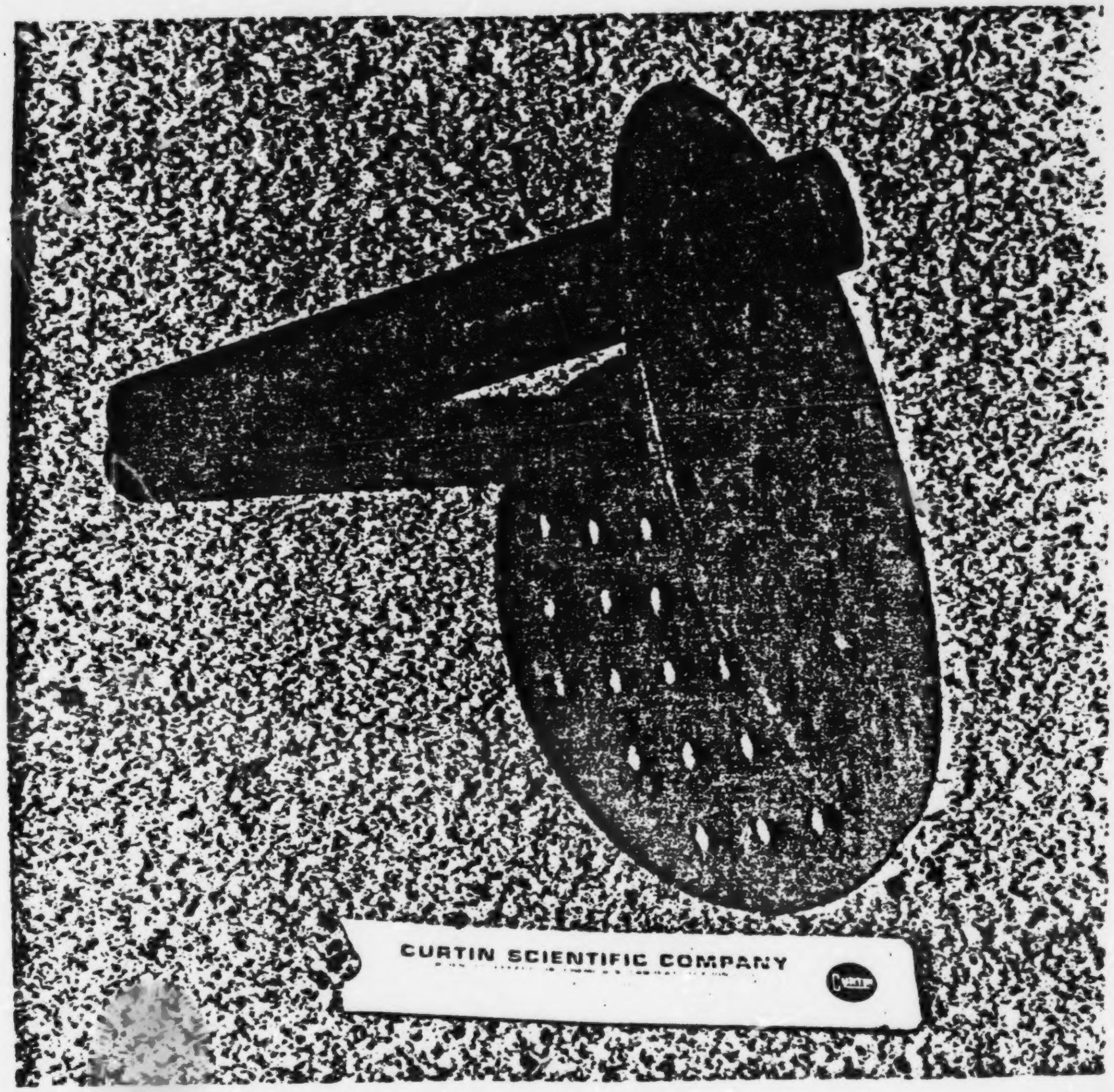
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Figure 13. Distilling column plate.

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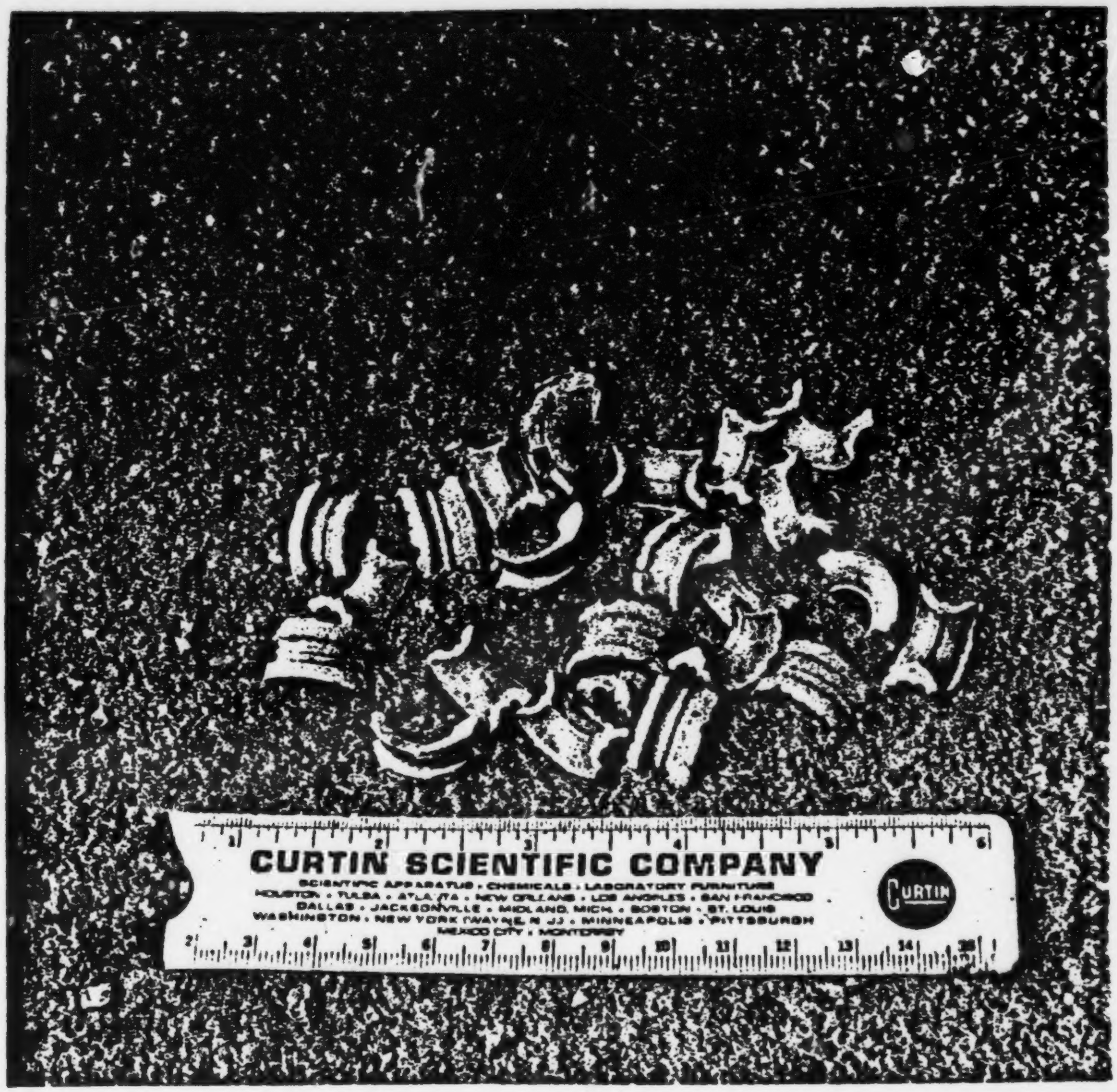
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Figure 14. Column packing.

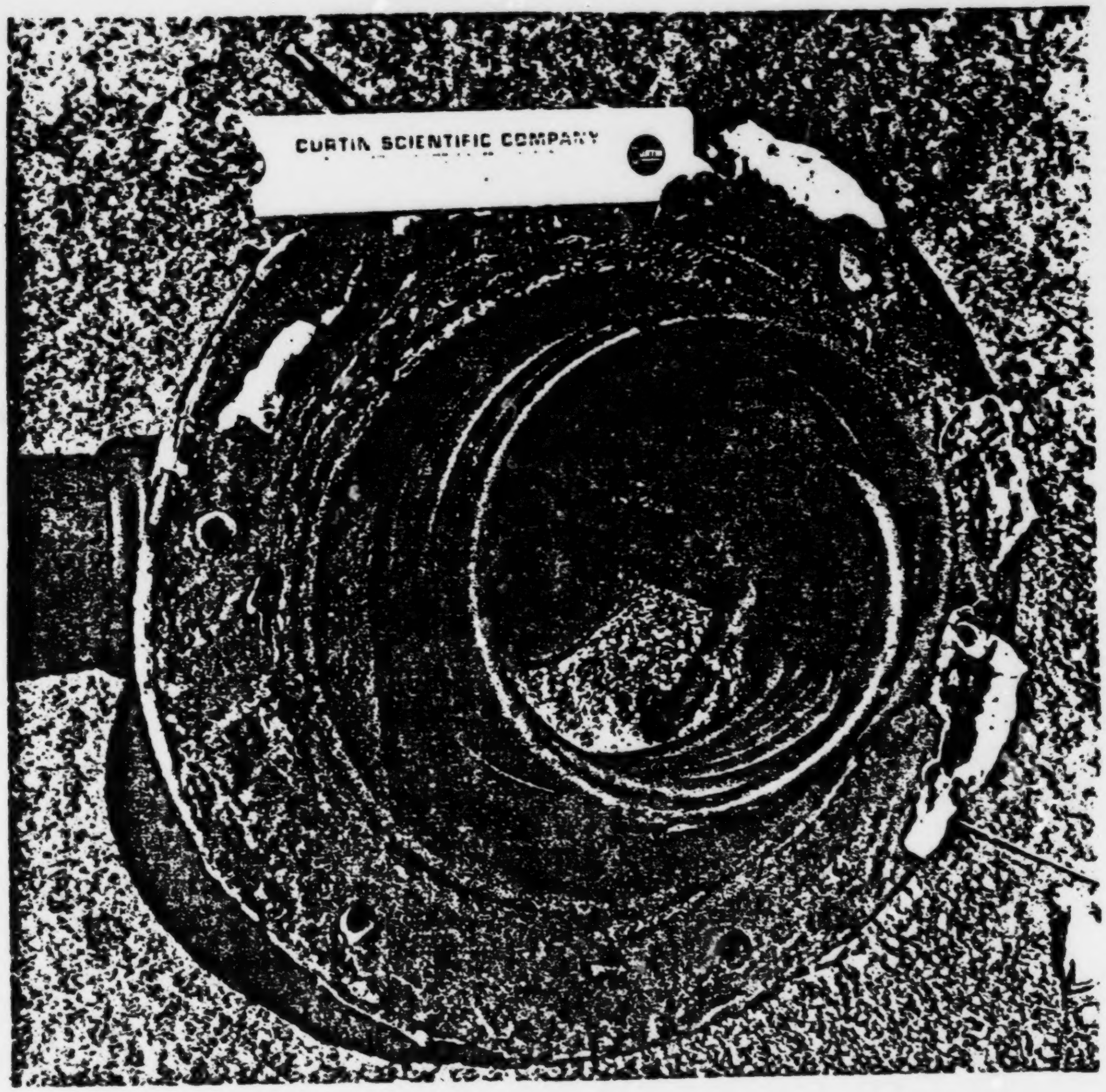
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Figure 15. Column top coding coil.

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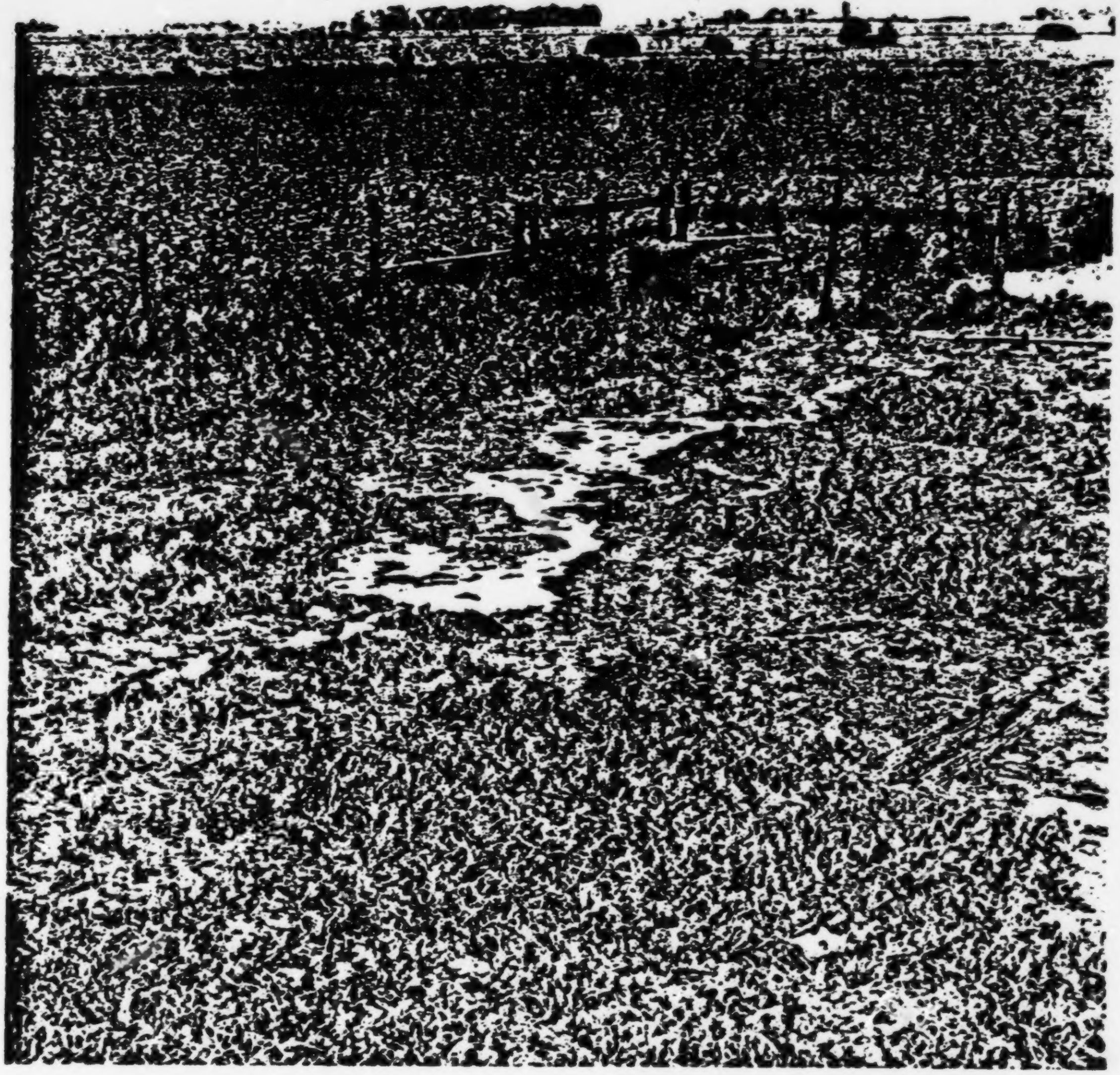

Figure 16. Washwater and beer bottoms drain area.

SECTION 3

SAMPLING TECHNIQUES

The purpose of the sampling effort at the two farms was to characterize all discharge and potential discharge streams throughout the process. All sampling equipment used was transported to and from the sites in the Acurex Emissions Monitoring Lab. The following paragraphs discuss the gaseous, solid, and liquid sampling techniques used.

3.1 GASEOUS EMISSIONS SAMPLING

The gaseous emissions, both vented and ambient, were sampled using the extractive system shown in Figure 17. The process emissions from the cooker/fermenter vent were monitored by drawing the sample gas through a stainless steel probe equipped with a thermocouple for gas temperature measurement, a filter, and condensate trap. The gas was then drawn through a length of heated Teflon sample line and pressurized by a Teflon-lined sample pump. The sample gas was then split into two portions, a hot/wet sample and a dry sample.

Drying the gas was effected by passing it through a moisture condenser. The dried gas was then split into two streams: one going directly to an oxygen monitor and the other through a diluter and on to the carbon dioxide monitor. The diluter used bottled nitrogen to dilute the gas sample to accommodate the range of the carbon dioxide analyzer.

The hot/wet sample gas was also split into two streams: one going to a total hydrocarbon monitor and the other to a gas chromatograph. The total hydrocarbon instrument monitored total hydrocarbons in the gas stream while the gas chromatograph speciated the components of the gas stream. Table 3 lists the compounds screened for by the gas chromatograph.

The gas velocity in the vent was measured by using a hot wire anemometer flow measuring device. The sensing probe was inserted upstream of the gas sampling probe.

The results of instrument measurements were logged on stripchart recorders. Table 4 lists the various monitors used, their characteristics, and calibration gases.

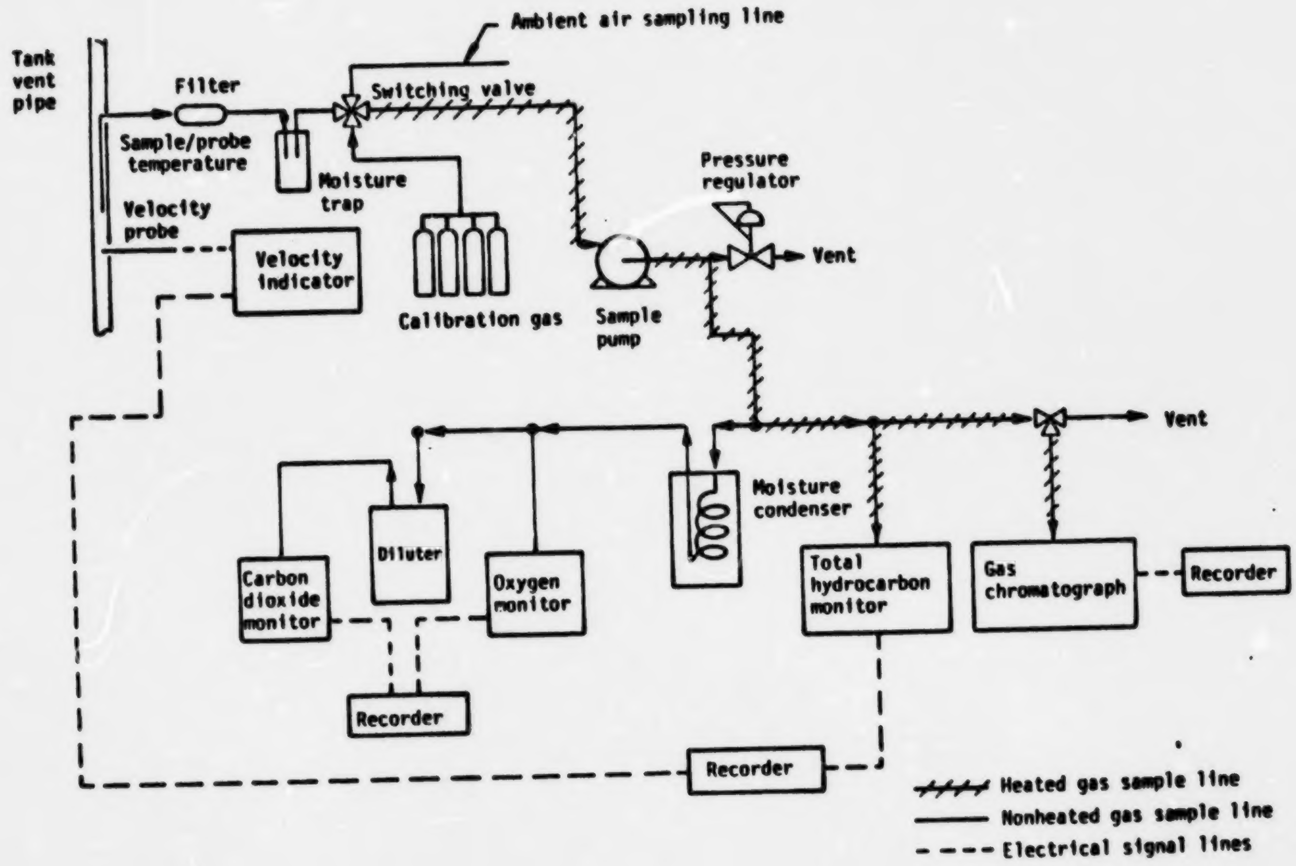
Ambient air sampling line
Tank vent pipe
Filter
Switching valve
Sample/probe temperature
Moisture trap
Velocity probe
Velocity indicator
Calibration gas
Pressure regulator
Vent
Sample pump
Vent
Moisture condenser
Diluter
Carbon dioxide monitor
Oxygen monitor
Total hydrocarbon monitor
Gas chromatograph
Recorder
Recorder
Recorder
Heated gas sample line
Nonheated gas sample line
Electrical signal lines

Figure 17. Gaseous sampling system.

TABLE 3. SPECIES SCREENED FOR BY GAS CHROMATOGRAPH

Alcohols

Methanol
Ethanol
1-propanol
2-propanol
1-butanol
2-butanol
2-methyl 1-propanol
2-methyl 2-propanol
1-pentanol
2-pentanol
3-pentanol
2-methyl 1-butanol
3-methyl 1-butanol
2-methyl 2-butanol

Aldehydes

Formaldehyde
Propionaldehyde
Butyraldehyde
Isobutyraldehyde
Valeraldehyde
Isovaleraldehyde
Furfuraldehyde

TABLE 4. GAS SAMPLING INSTRUMENTS

Instrument	Characteristics	Calibration/support gas
Oxygen monitor	Electrochemical fuel cell detector Ranges: 0-5, 0-10, 0-25 percent O_2	N_2, 8.1 percent O_2, ambient air
Diluter	Mechanical operation by capillary selection Dilution of 100 to 0, 10, 25, 40, 50, 70, 85	Nitrogen
Carbon dioxide monitor	Nondispersive infrared detector Range: 0-20 percent CO_2	N_2, 15.6 percent CO_2, 100 percent CO_2 (diluted)
Total hydrocarbon monitor	Flame ionization detector Ranges: 0-10, 100, 1000, 10,000 ppm	Zero air, H_2, 92 ppm CH_4, 8,199 ppm CH_4
Gas chromatograph	Flame ionization detector 6-ft Carbo-Pack SP-1000 column	Zero air, H_2, He, calibration standards (see Table 3)
Velocity indicator	Hot wire anemometer sensor Ranges of 0-300, 1,250, 6,000 FPM	None
Moisture condenser	Refrigeration type	None

Ambient air samples were taken by activating the switching valve on the sample line to the appropriate position and then moving the ambient sample line around the process building.

3.2 LIQUID AND SOLID SAMPLING

Liquid and solid samples were taken throughout the processes at the following points:

- Grain
- Make-up water
- Distillation feed
- Byproduct
- Beer bottoms
- Product
- Process washout
- Soil samples (Site B only)
- Redistilled beer bottoms (Site A only)

Table 5 lists these samples, the type of sample, and their sampling point.

TABLE 5. SOLID AND LIQUID SAMPLES AND ANALYSES REQUIRED

Description	Sample type	Sample point
Ground grain	Solid	Grain hopper
Make-up water	Liquid	Water pipe
Distillation feed	Liquid	Beer still inlet
Byproduct	Solid	Solid/liquid separator
Product	Liquid	Condenser outlet
Beer bottoms	Liquid	Beer still outlet
Process washout	Liquid	Drain pipe
Soil samples[a]	Solid	Drain area
Redistilled beer bottoms[b]	Liquid	Holding tank

[a] Site B only
[b] Site A only

After each of the samples were taken in their appropriate sample container and preserved, they were stored on ice for shipment to the Acurex laboratory. All of the samples, except for the product, were shipped on ice by an air carrier.

3.2.1 Grain Samples

The ground grain was sampled by taking a single grab sample from the hopper used to transport it from the grinding facility to the process site. After sampling, the container was sealed and put on ice.

3.2.2 Make-Up Water

Each of the two sites sampled had a water well, which was the only source for water used in the process. The water source was sampled just after the cooker tanks were filled with make-up water.

3.2.3 Distillation Feed

The distillation feed at both sites was sampled after the solid/liquid separation was performed. The various sample containers were filled, sealed, and then stored on ice for transport to the lab.

3.2.4 Byproduct

The byproduct was sampled after separation from the distillation feed by the solid/liquid separator. The samples were taken after the separator had been operating from awhile to ensure that no byproduct remained in the system from prior operation. These samples were stored on ice for shipment to the analysis lab.

3.2.5 Beer Bottoms

The beer bottoms were that portion of the distillation feed which remained after the alcohol was distilled from it in the beer still. The beer bottoms from Site A were to be trucked to a field and spread on the field. The beer bottoms from Site B were dumped on the ground as shown in Figure 16. The beer bottoms were sampled during the distilling process and then stored on ice.

The beer bottoms at Site A were stored in a tank truck until disposal. The head gas in the tank was field sampled and analyzed for ethanol content. The analysis indicated there was some alcohol remaining in the beer bottoms, so it was redistilled.

3.2.6 Product

The product, ethanol, was sampled at the outlet of the condensers. The sample was composited throughout the distillation since its proof changed when there were variations in the process temperature.

3.2.7 Process Washout

During the production of a batch of alcohol, various tanks, distilling columns, and heat exchangers were used. These were all washed down after their use. This washout water drained onto the ground around the ethanol facilities. The process washout water sample was a composite of all the washouts during the production of the ethanol. These samples were stored on ice after their sampling.

3.2.8 Soil Samples

During the process samplings, it was noted that the washout water or other process drainage caused the plant life to die in the drainage area (see Figure 16). Therefore, a sample of the soil void of plants, and a control sample of soil from the same field with plants growing, were taken. The soil sample was taken by scraping the top inch of soil into a sample container.

SECTION 4

ANALYTICAL TECHNIQUES

The sampling procedures discussed in Section 3 provided samples for detailed analyses in the laboratory. The analytical techniques employed were standard methods or optimized methods chosen from the available alternatives. In this section the methods used are summarized with references given for details.

The analytical scheme is divided into five tasks:

- Sample bottle preparation
- Sample preservation, shipping, and log-in
- Organics analyses
- General chemical tests
- Quality assurance/quality control

4.1 PREPARATION

All equipment and sample bottles were cleaned prior to use. Cleaning techniques generally include soap and water wash and deionized water rinse. Further special cleaning techniques depend on analytical requirements. High-temperature bake-outs, nitric and/or sulfuric acid washes, and nanograde solvent rinses are a few of these techniques. Field blanks assure the cleanliness of sample containers and equipment.

4.2 PRESERVATION, SHIPPING, AND LOG-IN

Liquid samples were screened for residual chlorine and pH in the field. Samples were then split and preserved according to Tables 6, 7, and 8. All samples were stored on ice at 4°C until receipt at the laboratory for analysis.

In conformance with the Federal Register of December 18, 1979, samples for BOD_5 were shipped on ice by commercial air carrier to the Acurex Mountain View Laboratory. The remainder of the samples were processed through the lab at the completion of the sampling program. Upon receipt at the laboratory, samples were logged in. This entailed:

- Issuing and recording lab identification number
- Recording sample label information

TABLE 6. LIQUID SAMPLES

Sampling point	Container/preservative
Make-up water	A, B, C, D, E, F, G
Beer bottoms (liquid waste)	A, B, C, D, E, F, G
Wash-out (a composite)	A, B, C, D, E, F, G
Product	G

TABLE 7. SOLID SAMPLES

Sampling point	Container/preservative
Ground grain	G
Distillation feed	F, G, A
Byproduct	G, A

TABLE 8. CONTAINER/PRESERVATIVE KEY

Code	Size	Wastewater preservative
A	2L	Plastic, no preservative
B	2L	Plastic, H_2SO_4 pH <2
C	2L	Plastic HNO_3 pH <2
D	1L	Plastic, NaOH pH >12
E	1L	Glass, $CuSO_4$ 1gm/1, H_3PO_4 pH <4
F	40 ml	VOA Vial, in duplicate
G	1 gal	Amber Glass, no preservative

- Noting condition of samples
- Date and time received
- Issuing sample tracking form

Immediately following sample log-in, samples were turned over to the organic and general chemistry laboratories.

The samples were received at Mountain View in lots on June 11, 18, 23, and July 2, 1980. Lot 3 was received 4 days after sampling at Site 2. As a result, the ice had melted and the temperature had risen to 10° to 15°C. The samples in this lot from Site B included the distillation feed, beer bottoms, washout water, solid byproduct, and soil runoff and control.

4.3 ANALYTICAL PROCEDURES

Methodologies used for organics analyses are based on EPA methods, the FDA Pesticide Analytical Manual, and Standard Methods for the Examination of Water and Wastewater 14th Ed. APHA, AWWA, WPCF. Aqueous samples were analyzed according to Table 9 and solid samples were analyzed according to Table 10.

TABLE 9. AQUEOUS SAMPLES

Analysis	Method
Extractable organics by GCMS	EPA 625
Volatile organics analysis (purge and trap)	EPA 624
Herbicides	Standard Method 509B

TABLE 10. SOLID ORGANIC ANALYSES

Analysis	Method	Note
Pesticides	FDA 211.13e	
Herbicides	FDA 222.13c	
Volatile organics analysis (purge and trap)	EPA 624	Dilute with organic-free water
Base/neutral and acid fraction	EPA 625	Soxhlet Extraction

Analytical methodologies used for the general chemistry analyses were based on Standard Methods for the Examination of Water and Wastewater 14th Ed. APHA, AWWA, WPCF, and Methods for the Analysis of Water and Wastes, EPA, March 1979. Aqueous samples were analyzed according to Table 11. The analytical procedures for high solids samples were basically the same as for the liquid samples (Table 11). Analyses of the soups generally entailed more sample preparation and more rigorous digestion.

The following is a summary of the test methods employed on the project samples. Following each method is a reference and brief description of the method.

1. Biochemical Oxygen Demand, BOD_{5day} (Ref. 1, Method 507)
   Portions of sample were incubated in the dark at 20°C for 5 days. Oxygen depletion was measured using an oxygen probe.

2. Chemical Oxygen Demand, COD (Ref. 1, Method 508)
   Samples were digested under reflex in a mixture of sulfuric acid and potassium dichromate. Dichromate consumption was measured.

3. Total Organic Carbon, TOC (Ref. 2, Method 415.1)
   Samples were analyzed on a Beckman 915 TOC Analyzer by Brown and Caldwell, Environmental Sciences Division. Organic carbon was converted to carbon dioxide and quantitated using an infrared detector.

4. pH Value (Ref. 1, Method 424)
   Samples were analyzed for pH using an Orion Model 701 pH meter. Solid samples were extracted with deionized water and the solution pH determined.

5. Specific Conductance (Ref. 1, Method 205)
   Sample conductivities were measured using a Lab-line Lectro Mho meter. The instrument measured the electrical conductivity of the sample.

6. Total Suspended Solids, TSS (Ref. 1, Method 208D)
   Samples were filtered and the residue on the filter was dried at 103° to 105°C. The gain in weight for a given volume was the total suspended solids.

7. Total Solids, TS (Ref. 1, Method 208A)
   Portions of the samples were dried at 103° to 105°C. The residue was determined gravimetrically.

8. Phenols (Ref. 1, Method 510A, 510B)
   Samples were distilled. The phenol in the distillate was reacted with 4 amino-antipyrine in the presence of potassium ferricyanide to form a colored antipyrine dye. The dye was extracted with chloroform. The concentration of extracted dye was determined spectrophotometrically.

TABLE 11. AQUEOUS GENERAL CHEMICAL ANALYSES

Analysis	Method
BOD_5	5-day incubation, sample analyzed for oxygen depletion
COD	Acid dichromate reflux, back titrate with ferrous ammonium sulfate
TOC	Conversion to CO_2, infrared quantitation
Total suspended solids	Gravimetric, 105°C, weigh residue on filters
Total solids	Gravimetric, 105°C, weigh residue
Phenols	Distill, amino antipyrine color, $CHCl_3$ extraction
Cyanides (total)	Distill, barbituric acid colorimetry
Ammonia	Distill, followed by nesslerization
Nitrate	Brucine colorimetric
Sulfate	Turbidimetric
Phosphorous	Nitric/sulfuric acid digest, ascorbic acid colorimetry
Specific conductance	Wheatstone bridge conductivity
Metals	Atomic absorption spectrophotometry following acid digestion. Analysis by cold-vapor flameless AA (Hg), flame and graphite furnace analyses as appropriate for others
pH	Electrometric
Total Kjeldahl nitrogen	Sulfuric acid mercuric oxide digestion, distillation, nesslerization

Metals: Al, Sb, As, Ba, Be, Bi, Cd, Ca, Cu, Cr, Fe, Pb, Mg, Mn, Hg, Ni, Se, Ag, Tl, Ti, and Zn

9. Cyanide (Ref. 1, Method 413A, B, D)
   The cyanide content of the samples was determined following the preliminary distillation of HCN from an acidified sample. The HCN was absorbed in a NaOH solution. The NaOH solution was analyzed for cyanide using the pyridine barbituric acid colorimetric method.

10. Ammonia Nitrogen (Ref. 1, Method 418A, B)
   Samples were distilled from buffered basic solution into boric acid absorbant. The distillates were analyzed for ammonia content using the nesslerization (colorimeter) method.

11. Total Kjeldahl Nitrogen (Ref. 1, Method 421)
   Samples were digested with a mixture of sulfuric acid, mercuric oxide and potassium sulfate. This released most amino nitrogens. The ammonia was then distilled from the solution and absorbed in boric acid. The distillates were analyzed using the nesslerization method.

12. Nitrate Nitrogen (Ref. 1, Method 419D)
   Nitrates were determined using the Brucine colorimetric method. Solid or high suspended solid samples were extracted with dilute sulfuric acid and filtered preceeding analysis.

13. Sulfate (Ref. 1, Method 427C)
   Sulfates were determined turbidimetrically. Solid or high suspended solid samples were refluxed with dilute hydrochloric acid and filtered preceeding analysis. Sulfate content was determined by mixing portions of the extract with conditioning reagent. Barium chloride crystals were added and the barium sulfate crystals formed were quantitated using a nephelometer.

14. Phosphates, Total (Ref. 1, Method 425C, F)
   Samples were digested in nitric and sulfuric acids to release organically bound phosphorus. Following digestion, phosphorus was determined using ascorbic acid colorimetry.

15. Metals, Total
   Metals were determined by atomic absorption spectrophotometry. Samples were digested with nitric acid. Mercury was determined by the cold vapor technique. Other metals were determined by either flame or graphite furnace atomization of the acid digest. A Perkin-Elmer Model 460 atomic absorption spectrophotometer equipped with a Model 2100 Controller and Ramp Accessory and auto sampling system was used.

   Table 12 lists the method reference for each of the metals. Deviations from the standard procedures were adaptations to the nature of the samples submitted. Deviations were primarily in quantities and final concentrations of acid in the prepared samples.

TABLE 12. ANALYSIS METHOD FOR METALS DETERMINATION

Metal	Reference	Method
Aluminum	2	202.1
Antimony	2	204.2
Arsenic	2	206.2
Barium	2	208.1, 208.2
Beryllium	2	210.1, 210.2
Bismuth	3	Flame/furnace
Cadmium	2	213.1, 213.2
Calcium	2	215.1
Chromium	2	218.1, 218.2
Copper	2	220.1, 220.2
Iron	2	236.1
Lead	2	239.1, 239.2
Magnesium	2	242.1
Manganese	2	243.1, 243.2
Mercury	2	245.1
Nickel	2	249.1
Selenium	2	270.2
Silver	2	272.1, 272.2
Thallium	2	279.2
Titanium	2	283.1, 283.2
Zinc	2	289.1

16. Volatile Organics Analysis, VOA (Ref. 4, EPA Method 624)
Volatile organics were determined by the purge and trap technique. Basically, volatile compounds were purged with helium and adsorbed on a Tenax® trap. The volatile compounds were then desorbed onto a carbopack GC column where they were identified and quantitated by a Finnigan Model 4000 mass spectrometer.

17. Ethanol (Ref. 4, EPA Method 624, modified)
Ethanol was quantitated by gas chromatography using a flame ionization detector. Ethanol was separated from other compounds on a Carbopack column.

18. Base Neutral/Acid Priority Pollutants (Ref. 4, EPA Method 625)
Base neutral and acid priority pollutants were extracted from fluid and solid samples by continuous liquid-liquid extraction.

The sample (1.0 liter for water samples, 0.5 liter for distillation feed samples and 50 gm for byproduct samples) was diluted to 2.0 liters, basified to pH 14, spiked with surrogate standards (100 micrograms) and extracted overnight with dichloro methane. The sample was then adjusted to a pH of 1.0 and the acids were extracted with fresh solvent the following night. Analysis of the samples continued as per EPA Method 625.

19. Pesticides and Herbicides
Samples of feed grain were soxhlet extracted overnight with hexane/ether (50/50). The extracts were separated into pesticide and herbicide fractions by extracting the hexane/ether with dilute sodium hydroxide. The pesticide fraction was cleaned up and analyzed for chlorinated pesticides as described in the FDA Pesticide Analytical Manual (Reference 5). Herbicides were analyzed by the standard BF_3-methanol esterification (Reference 6) procedure followed by gas chromatography and electron capture detection.

SECTION 5

ANALYTICAL RESULTS AND DISCUSSION

The laboratory and field analytical results are presented and discussed in this section. A brief description of the quality control procedures is also included. The actual results for precision, accuracy, and recovery experiments are given in Appendix A. The results presented are not revised for the percent recoveries determined.

5.1 LABORATORY ANALYTICAL RESULTS

The laboratory analytical sample matrix is shown in Table 13. The results for Site A are given in Tables 14 to 19 and for Site B in Tables 20 to 25. Table 26 gives the ethanol content in the various streams.

The data is organized as follows:

- Conventional parameters
- Metals, cyanide, and phenols
- Priority pollutants
    - Acid compounds
    - Base/neutral compounds
    - Volatile organics
    - Pesticides and herbicides

5.2 DISCUSSION OF RESULTS

The process waste streams (beer bottoms and washout water) exhibited certain common characteristics of high BOD_5, COD, TSS and TOC, and low pH (acidic).

Solids and oxygen demand were extremely high but decreased over time through the system (see Tables 14 and 20). The analytical values for Site B are probably on the low side because of the warming of the samples in transit. Laboratory analyses indicated that most of the substances contributing to oxygen demand were biodegradeable.

Discharge of these materials would most severely affect oxygen-sensitive areas such as surface waters. Dissolved oxygen is a fundamental requirement of life for the plant and animal population in any given body of water. Their survival depends upon the ability of the water to maintain certain minimal concentrations of oxygen. The primary cause of water

TABLE 13. ANALYTICAL MATRIX
(The following analyses were performed on the project samples)

Site	Sample type	BOD_5	COD	TOC	pH	Conductivity	TSS	TS	Phenol	Cyanide	NH_3 TKN	NO_3	SO_4	PO_4	Metals[a]	VOA	BN/A	Pesticides	Herbicides	EtOH
A	Make-up water	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			
	Feed grain																	X	X	
	Distillation feed	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
	Beer bottoms	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
	Washout water	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
	Byproduct				X			X	X	X	X	X	X	X	X		X			X
	Product																			X
	Cooker runoff				X															X
B	Make-up water	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			
	Feed Grain																	X	X	
	Distillation feed	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
	Beer bottoms	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
	Washout water	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
	Byproduct				X			X	X	X	X	X	X	X	X	X	X			X
	Product																			X
	Soil				X						X	X		X						
	Soil control				X						X	X		X						

[a] Al, Sb, As, Ba, Be, Bi, Cd, Ca, Cu, Cr, Fe, Pb, Mg, Mn, Hg, Ni, Se, Ag, Tl, Ti, Zn

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TABLE 14. ANALYSIS RESULTS -- CONVENTIONAL PARAMETERS SITE A
(Units are mg/L unless noted otherwise)

Stream Parameter	Make-up water	Distillation feed	Beer bottoms	Redistilled beer bottoms	Washout water	Byproduct	Cooker mash runoff
Biochemical oxygen demand (BOD_5)	<2	127,000 mg/kg	27,500	--[a]	37,000	--	--
Chemical oxygen demand (COD)	72	114,000	61,000	50,000	37,000	--	--
Total organic carbon (TOC)	36	44,200	16,200	9,500	9,500	--	--
pH, electrometric at 25°C	7.15	4.00	4.0	--	3.90	3.9	5.8
Specific conductance micromhos/cm at 25°C	850	3,800	3,550	--	3,400	--	--
Total suspended solids 103-105°C (TSS)	9	20,000	15,000	--	14,000	--	--
Total solids 103-105°C (TS)	570	35,500	26,500	--	19,000	33%[a]	--
NH_3 as N	0.07	15	19	27	32	34 mg/kg	--
Total kjeldahl nitrogen (TKN)	≤0.1	1,980	1,350	410	500	1.65%[a]	--
SO_4	93	<5	35	--	74	<40 mg/kg	--
P	0.29	340	310	215	91	1,250 mg/kg	--
NO_3	<0.05	3	3.6	3.6	2.0	5 mg/kg	--

--Not requested
[a] Percent by weight

TABLE 15. RESULTS OF METALS, CYANIDE, AND PHENOLS -- SITE A

Parameter	Make-up water	Distillation feed	Beer bottoms	Washout water	Byproduct
Units	mg/L	mg/L	mg/L	mg/L	mg/kg
Aluminum, Al	<1.0	<1.0	1.0	1.0	<1.0
Antimony, Sb	<0.02	<0.02	<0.02	<0.02	<0.2
Arsenic, As	<0.02	<0.02	<0.02	<0.02	<0.2
Barium, Bq	<0.5	<0.5	<0.5	<0.5	<5.0
Beryllium, Be	<0.001	<0.02	<0.02	<0.02	<0.2
Bismuth, Bi	<0.03	<0.1	<0.1	<0.1	<1.0
Cadmium, Cd	<0.002	0.005	0.003	0.003	<0.02
Calcium, Ca	135.0	66.0	92.0	137.0	220.0
Chromium, Cr	<0.003	<0.05	0.1	0.05	0.5
Copper, Cu	<0.002	0.25	0.36	0.36	3.2
Iron, Fe	2.88	17.0	86.0	34.5	92.0
Lead, Pb	<0.005	<0.3	<0.3	<0.3	<3.0
Magnesium, Mg	23.5	120.0	170.0	84.0	270.0
Manganese, Mn	1.25	1.25	2.1	1.5	4.6
Mercury, Hg	<0.001	<0.002	<0.002	<0.002	<0.02
Nickel, Ni	0.02	<0.1	<0.1	<0.1	<1.0
Selenium, Se	<0.01	<0.02	<0.02	<0.02	<0.2
Silver, As	<0.001	<0.001	≤0.001	<0.001	<0.02
Thallium, Tl	<0.005	<0.02	<0.02	<0.02	<0.2
Titanium, Ti	<0.01	≤0.04	<0.04	0.04	0.7
Zinc, Zn	<0.01	2.6	4.0	1.79	6.7
Cyanide, CN	<0.01	<0.01	<0.01	<0.01	<0.1
Phenols, as C_6H_6O	0.05	0.09	0.08	0.05	≤0.2

TABLE 16. PRIROITY POLLUTANT ANALYSIS: ACID COMPOUNDS ($\mu g/L$) -- SITE A

	Acid compounds	Distillation feed	Beer bottoms	Washout water	Byproduct[a]	Make-up water	Detection limits
21A	2,4,6-trichlorophenol	ND	ND	ND	ND	ND	20
22A	p-chloro-m-cresol	ND	ND	ND	ND	ND	20
24A	2-chlorophenol	ND	ND	ND	ND	ND	20
31A	2,4-dichlorophenol	ND	ND	ND	ND	ND	20
34A	2,4-dimethylphenol	ND	ND	T[b]	ND	ND	20
57A	2-nitrophenol	ND	ND	ND	ND	ND	20
58A	4-nitrophenol	ND	ND	ND	ND	ND	50
59A	2,4-dinitrophenol	ND	ND	ND	ND	ND	100
60A	4,6-dinitro-o-cresol	ND	ND	ND	ND	ND	100
64A	pentachlorophenol	ND	ND	ND	ND	ND	20
65A	phenol	ND	ND	ND	ND	ND	20

ND = Not detected

[a] Unit are $\mu g/g$ and detection limit is 10 times value shown.

[b] T = Trace (present but not quantifiable)

TABLE 17. PRIORITY POLLUTANT ANALYSIS: BASE/NEUTRAL COMPOUNDS (μg/L) -- SITE A

Base/neutral compounds		Distillation feed	Beer bottoms	Washout water	Byproduct[a]	Make-up water	Detection limits
1B	acenaphthene	ND	ND	ND	ND	ND	1
5B	benzidine	ND	ND	ND	ND	ND	50
8B	1,2,4-trichlorobenzene	ND	ND	ND	ND	ND	10
9B	Hexachlorobenzene	ND	ND	ND	ND	ND	10
12B	Hexachloroethane	ND	ND	ND	ND	ND	10
18B	bis(2-chloroethyl)ether	ND	ND	ND	ND	ND	10
20B	2-chloronaphthalene	ND	ND	ND	ND	ND	10
25B	1,2-dichlorobenzene	ND	ND	ND	ND	ND	10
26B	1,3-dichlorobenzene	ND	ND	ND	ND	ND	10
27B	1,4-dichlorobenzene	ND	ND	ND	ND	ND	10
28B	3,3'-dichlorobenzidine	ND	ND	ND	ND	ND	10
35B	2,4-dinitrotoluene	ND	ND	ND	ND	ND	10
36B	2,6-dinitrotoluene	ND	ND	ND	ND	ND	10
37B	1,2-diphenylhydrazine (as azobenzene)	ND	ND	ND	ND	ND	10
39B	fluoranthene	ND	ND	8	ND	ND	1
40B	4-chlorophenyl phenylether	ND	ND	ND	ND	ND	10
41B	4-bromophenyl phenyl ether	ND	ND	ND	ND	ND	10
42B	bis(2-chloroisopropyl)ether	ND	ND	ND	ND	ND	10
43B	bis(2-chloroethoxy)methane	ND	ND	ND	ND	ND	10
52B	hexachlorobutadiene	ND	ND	ND	ND	ND	10
53B	hexachlorocyclopentadiene	ND	ND	ND	ND	ND	NA
54B	isophorone	ND	ND	ND	ND	ND	10
55B	naphthalene	ND	ND	ND	ND	ND	1
56B	nitrobenzene	ND	ND	ND	ND	ND	10
61B	N-nitrosodimethylamine	ND	ND	ND	ND	ND	NA
62B	N-nitrosodiphenylamine	ND	ND	ND	ND	ND	10
63B	N-nitrosodi-n-propylamine	ND	ND	ND	ND	ND	10

Continued

ND = Not detected

[a] Unit are μg/g and detection limit is 10 times value shown.

TABLE 17. Concluded

Base/neutral compounds	Distillation feed	Beer bottoms	Washout water	Byproduct[a]	Make-up water	Detection limits
66B bis(2-ethylhexyl) phthalate	ND	ND	ND	ND	ND	10
68B di-n-butyl phthalate	ND	ND	ND	ND	ND	10
69B di-n-octyl phthalate	ND	ND	ND	ND	ND	10
70B diethyl phthalate	ND	ND	ND	ND	ND	10
71B dimethyl phthalate	ND	ND	ND	ND	ND	10
72B benzo(a)anthracene	ND	ND	ND	ND	ND	1
73B benzo(a)pyrene	ND	ND	ND	ND	ND	1
74B 3,4-benzofluoranthene	ND	ND	ND	ND	ND	1
75B Benzo(k)fluoranthene	ND	ND	ND	ND	ND	1
76B crysene	ND	ND	ND	ND	ND	1
77B acenaphthylene	ND	ND	ND	ND	ND	1
78B anthracene	ND	ND	ND	ND	ND	1
79B benzo(ghi)perylene	ND	ND	ND	ND	ND	20
80B fluorene	ND	ND	ND	ND	ND	1
81B phenanthrene	ND	ND	3	ND	ND	1
82B dibenzo(a,h)anthracene	ND	ND	ND	ND	ND	20
83B indeno(1,2,3-cd)pyrene	ND	ND	ND	ND	ND	20
84B pyrene	ND	ND	3	ND	ND	1

ND = Not detected
[a] Unit are μg/g and detection limit is 10 times value shown.

TABLE 18. PRIORITY POLLUTANT ANALYSIS: VOLATILE ORGANICS (µg/L) -- SITE A

Base/neutral compounds		Distillation feed	Beer bottoms	Washout water	Make-up water	Detection limits
2V	acrolein	ND	ND	ND	ND	100
3V	acrylonitrile	ND	ND	ND	ND	100
4V	benzene	ND	ND	ND	13[a]	10
6V	carbon tetrachloride	ND	ND	ND	ND	10
7V	chlorobenzene	ND	ND	ND	ND	5
10V	1,2-dichloroethane	ND	ND	ND	ND	10
11V	1,1,1-trichloroethane	ND	ND	ND	ND	10
13V	1,1-dichloroethane	ND	ND	ND	ND	10
14V	1,1,2-trichloroethane	ND	ND	ND	ND	10
15V	1,1,2,2-tetrachloroethane	ND	ND	ND	ND	10
16V	chloroethane	ND	ND	ND	ND	50
19V	2-chloroethylvinyl ether	ND	ND	ND	ND	50
23V	chloroform	ND	ND	ND	ND	10
29V	1,1-dichloroethylene	ND	ND	ND	ND	10
30V	1,2-trans-dichloroethylene	ND	ND	ND	ND	10
32V	1,2-dichloropropane	ND	ND	ND	ND	10
33V	1,3-dichloropropylene	ND	ND	ND	ND	10
38V	ethylbenzene	ND	ND	ND	ND	5
44V	methylene chloride	ND	ND	150[b]	34[b]	50
45V	methyl chloride	ND	ND	ND	ND	50
46V	methyl bromide	ND	ND	ND	ND	50
47V	bromoform	ND	ND	ND	ND	10
48V	dichlorobromomethane	ND	ND	ND	ND	10
49V	trichlorofluormethane	ND	ND	ND	ND	10
50V	dichlorodifluoromethane	ND	ND	ND	ND	50
51V	chlorodibromomethane	ND	ND	ND	ND	10
85V	tetrachloroethylene	ND	ND	ND	ND	10
86V	toluene	ND	ND	ND	ND	10
87V	trichlorethylene	ND	ND	ND	ND	10
88V	vinyl chloride	ND	ND	ND	ND	50

ND = Not detected
[a] Possible lab contamination
[b] Probable lab contamination

TABLE 19. PRIORITY POLLUTANT ANALYSIS: FEED GRAIN (μg/L) -- SITE A

Priority pollutant			
Herbicides	2,4-dichlorophenoxyacetic acid		ND
	2,4,5-trichlorophenoxyacetic acid		ND
	Silvex		0.016
Pesticides	89P	aldrin	ND
	90P	dieldrin	ND
	91P	chlordane	ND
	92P	4,4'-DDT	ND
	93P	4,4'-DDE	ND
	94P	4,4'-DDD	ND
	95P	α-endosulfan	ND
	96P	β-endosulfan	ND
	97P	endosulfan sulfate	ND
	98P	endrin	ND
	99P	endrin aldehyde	ND
	100P	heptachlor	0.0005
	101P	heptachlor epoxide	ND
	102P	α-BHC	ND
	103P	β-BHC	ND
	104P	δ-BHC	ND
	105P	γ-BHC	ND
	106P	PCB-1242	ND
	107P	PCB-1254	ND
	108P	PCB-1221	ND
	109P	PCB-1232	ND
	110P	PCB-1248	ND
	111P	PCB-1260	ND
	112P	PCB-1016	ND
	113P	toxaphene	ND

ND = Not detected

TABLE 20. ANALYSIS RESULTS -- CONVENTIONAL PARAMETERS SITE B (Units are mg/L unless noted otherwise)

Stream Parameter	Make-up water	Distillation feed	Beer bottoms	Washout Water	Byproduct	Soil	Soil control
BOD_5	<2	83,000	50,500	18,500	--[a]	--	--
COD	<5	105,000	72,000	44,000	--	--	--
TOC	16	35,000	20,700	8,400	--	--	--
pH, electrometric at 25°C	6.85	3.55	3.70	3.65	3.40	6.00	6.60
Specific conductance micromhos/cm at 25°C	560	4,700	4,050	1,700	--	--	--
TSS, 103-105°C	<5	11,500	12,000	8,400	--	--	--
TS 103-105°C	350	30,000	19,000	13,000	21%[a]	--	--
NH_3 as N	<0.1	10	13	53	66 mg/kg	0.06%[a]	0.03%[a]
TKN	0.4	990	780	370	1.16%[a]	0.76%[a]	0.48%[a]
SO_4	55	(520)[b]	330	76	740 mg/kg	--	--
P	0.1	380	240	82	910	0.017%[a]	0.020[a]
NO_3	2.3	3.4	5.0	3.0	13 mg/kg	0.01%[a]	0.008%[a]

--Not requested

[a] Percent by weight

[b] Wide variation in measurements

TABLE 21. RESULTS OF METALS, CYANIDE, AND PHENOLS -- SITE B

Parameter	Make-up water	Distillation feed	Beer bottoms	Washout water	Byproduct
Units	mg/L	mg/L	mg/L	mg/L	mg/kg
Aluminum, Al	<1.0	1.3	1.0	1.3	<10.0
Antimony, Sb	<0.02	<0.02	<0.02	<0.02	<0.2
Arsenic, As	<0.02	<0.02	<0.02	<0.02	<0.2
Barium, Bq	<0.5	<0.5	<0.5	<0.5	<5.0
Beryllium, Be	<0.001	<0.02	<0.02	<0.02	<0.2
Bismuth, Bi	<0.1	<0.1	<0.1	<0.1	<1.0
Cadmium, Cd	<0.002	0.004	0.006	0.002	<0.02
Calcium, Ca	59.5	150.0	139.0	120.0	230.0
Chromium, Cr	<0.003	<0.05	<0.05	0.05	<0.5
Copper, Cu	1.32	0.76	4.72	1.11	5.1
Iron, Fe	≤0.05	64.0	134.0	39.6	128.0
Lead, Pb	<0.005	<0.3	<0.3	<0.3	<3.0
Magnesium, Mg	10.0	210.0	150.0	56.0	210.0
Manganese, Mn	≤0.02	1.5	1.9	0.77	3.9
Mercury, Hg	<0.001	<0.002	<0.002	<0.002	<0.02
Nickel, Ni	<0.01	<0.1	<0.1	<0.1	<1.0
Selenium, Se	<0.01	<0.02	<0.02	<0.02	<0.2
Silver, As	<0.001	<0.001	<0.001	<0.001	<0.02
Thallium, Tl	<0.005	<0.02	<0.02	<0.02	<0.2
Titanium, Ti	<0.01	<0.04	<0.04	≤0.04	<0.4
Zinc, Zn	0.25	3.9	7.3	3.3	16.7
Cyanide, CN	<0.01	<0.01	<0.01	<0.01	<0.1
Phenols, as C_6H_6O	<0.05	0.07	0.08	<0.05	<0.2

TABLE 22. PRIORITY POLLUTANT ANALYSIS: ACID COMPOUNDS (μg/L) -- SITE B

Acid compounds	Distillation feed	Beer bottoms	Washout water	Byproduct[a]	Make-up water	Detection limits
21A 2,4,6-trichlorophenol	ND	ND	ND	ND	ND	20
22A p-chloro-m-cresol	ND	ND	ND	ND	ND	20
24A 2-chlorophenol	ND	ND	ND	ND	ND	20
31A 2,4-dichlorophenol	ND	ND	ND	ND	ND	20
34A 2,4-dimethylphenol	ND	ND	T[b]	ND	ND	20
57A 2-nitrophenol	ND	ND	ND	ND	ND	20
58A 4-nitrophenol	ND	ND	ND	ND	ND	50
59A 2,4-dinitrophenol	ND	ND	ND	ND	ND	100
60A 4,6-dinitro-o-cresol	ND	ND	ND	ND	ND	100
64A pentachlorophenol	ND	ND	ND	ND	ND	20
65A phenol	ND	ND	ND	ND	ND	20

ND = Not detected

[a] Units are μg/g and detection limit is 10 times value shown.

[b] T = trace (present but not quantifiable)

TABLE 23. PRIORITY POLLUTANT ANALYSIS: BASE/NEUTRAL COMPOUNDS (μg/L) -- SITE B

Base/neutral compounds		Distillation feed	Beer bottoms	Washout water	Byproduct[a]	Make-up water	Detection limits
1B	acenaphthene	ND	ND	ND	ND	ND	1
5B	benzidine	ND	ND	ND	ND	ND	50
8B	1,2,4-trichlorobenzene	ND	ND	ND	ND	ND	10
9B	Hexachlorobenzene	ND	ND	ND	ND	ND	10
12B	Hexachloroethane	ND	ND	ND	ND	ND	10
18B	bis(2-chloroethyl)ether	ND	ND	ND	ND	ND	10
20B	2-chloronaphthalene	ND	ND	ND	ND	ND	10
25B	1,2-dichlorobenzene	ND	ND	ND	ND	ND	10
26B	1,3-dichlorobenzene	ND	ND	ND	ND	ND	10
27B	1,4-dichlorobenzene	ND	ND	ND	ND	ND	10
28B	3,3'-dichlorobenzidine	ND	ND	ND	ND	ND	10
35B	2,4-dinitrotoluene	ND	ND	ND	ND	ND	10
36B	2,6-dinitrotoluene	ND	ND	ND	ND	ND	10
37B	1,2-diphenylhydrazine (as azobenzene)	ND	ND	ND	ND	ND	10
39B	fluoranthene	ND	ND	ND	ND	ND	1
40B	4-chlorophenyl phenylether	ND	ND	ND	ND	ND	10
41B	4-bromophenyl phenyl ether	ND	ND	ND	ND	ND	10
42B	bis(2-chloroisopropyl)ether	ND	ND	ND	ND	ND	10
43B	bis(2-chloroethoxy)methane	ND	ND	ND	ND	ND	10
52B	hexachlorobutadiene	ND	ND	ND	ND	ND	10
53B	hexachlorocyclopentadiene	ND	ND	ND	ND	ND	NA
54B	isophorone	ND	ND	ND	ND	ND	10
55B	naphthalene	ND	ND	ND	ND	ND	1
56B	nitrobenzene	ND	ND	51	ND	ND	10
61B	N-nitrosodimethylamine	ND	ND	ND	ND	ND	NA
62B	N-nitrosodiphenylamine	ND	ND	ND	ND	ND	10
63B	N-nitrosodi-n-propylamine	ND	ND	ND	ND	ND	10

Continued

ND = Not detected

[a] Units are μg/g and detection limit is 10 times value shown.

TABLE 23. Concluded

Base/neutral compounds	Distillation feed	Beer bottoms	Washout water	Byproduct[a]	Make-up water	Detection limits
66B bis(2-ethylhexyl) phthalate	ND	ND	ND	ND	ND	10
68B di-n-butyl phthalate	ND	ND	ND	ND	ND	10
69B di-n-octyl phthalate	ND	ND	ND	ND	ND	10
70B diethyl phthalate	ND	ND	ND	ND	ND	10
71B dimethyl phthalate	ND	ND	ND	ND	ND	10
72B benzo(a)anthracene	ND	ND	ND	ND	ND	1
73B benzo(a)pyrene	ND	ND	ND	ND	ND	1
74B 3,4-benzofluoranthene	ND	ND	ND	ND	ND	1
75B Benzo(k)fluoranthene	ND	ND	ND	ND	ND	1
76B crysene	ND	ND	ND	ND	ND	1
77B acenaphthylene	ND	ND	ND	ND	ND	1
78B anthracene	ND	ND	ND	ND	ND	1
79B benzo(ghi)perylene	ND	ND	ND	ND	ND	20
80B fluorene	ND	ND	ND	ND	ND	1
81B phenanthrene	ND	ND	ND	ND	ND	1
82B dibenzo(a,h)anthracene	ND	ND	ND	ND	ND	20
83B indeno(1,2,3-cd)pyrene	ND	ND	ND	ND	ND	20
84B pyrene	ND	ND	ND	ND	ND	1

ND = Not detected

[a] Units are μg/g and detection limit is 10 times value shown.

TABLE 24. PRIORITY POLLUTANT ANALYSIS: VOLATILES, ORGANICS (μg/L) -- SITE B

	Volatiles	Distillation feed	Beer bottoms	Washout water	Make-up water	Detection limits
2V	acrolein	ND	ND	ND	ND	100
3V	acrylonitrile	ND	ND	ND	ND	100
4V	benzene	ND	ND	ND	ND	10
6V	carbon tetrachloride	ND	ND	ND	ND	10
7V	chlorobenzene	ND	ND	ND	ND	5
10V	1,2-dichloroethane	ND	ND	ND	ND	10
11V	1,1,1-trichloroethane	ND	ND	ND	ND	10
13V	1,1-dichloroethane	ND	ND	ND	ND	10
14V	1,1,2-trichloroethane	ND	ND	ND	ND	10
15V	1,1,2,2-tetrachloroethane	ND	ND	ND	ND	10
16V	chloroethane	ND	ND	ND	ND	50
19V	2-chloroethylvinyl ether	ND	ND	ND	ND	50
23V	chloroform	ND	ND	ND	ND	10
29V	1,1-dichloroethylene	ND	ND	ND	ND	10
30V	1,2-trans-dichloroethylene	ND	ND	ND	ND	10
32V	1,2-dichloropropane	ND	ND	ND	ND	10
33V	1,3-dichloropropylene	ND	ND	ND	ND	10
38V	ethylbenzene	ND	ND	ND	ND	5
44V	methylene chloride[a]	54[b]	ND	1300[b]	54[b]	50
45V	methyl chloride	ND	ND	ND	ND	50
46V	methyl bromide	ND	ND	ND	ND	50
47V	bromoform	ND	ND	ND	ND	10
48V	dichlorobromomethane	ND	ND	ND	ND	10
49V	trichlorofluormethane	ND	ND	ND	ND	10
50V	dichlorodifluoromethane	ND	ND	ND	ND	50
51V	chlorodibromomethane	ND	ND	ND	ND	10
85V	tetrachloroethylene	ND	ND	ND	ND	10
86V	toluene	ND	ND	ND	ND	10
87V	trichlorethylene	ND	ND	ND	ND	10
88V	vinyl chloride	ND	ND	ND	ND	50

ND = Not detected

[a] Common lab contaminent

[b] Probable contamination

TABLE 25. PRIORITY POLLUTANT ANALYSIS: FEED GRAIN (μg/L) -- SITE B

	Priority pollutant		
Herbicides	2,4-dichlorophenoxyacetic acid		ND
	2,4,5-trichlorophenoxyacetic acid		ND
	Silvex		ND
Pesticides	89P	aldrin	ND
	90P	dieldrin	ND
	91P	chlordane	ND
	92P	4,4'-DDT	ND
	93P	4,4'-DDE	ND
	94P	4,4'-DDD	ND
	95P	α-endosulfan	ND
	96P	β-endosulfan	ND
	97P	endosulfan sulfate	ND
	98P	endrin	ND
	99P	endrin aldehyde	ND
	100P	heptachlor	0.0002
	101P	heptachlor epoxide	ND
	102P	α-BHC	ND
	103P	β-BHC	ND
	104P	δ-BHC	ND
	105P	γ-BHC	ND
	106P	PCB-1242	ND
	107P	PCB-1254	ND
	108P	PCB-1221	ND
	109P	PCB-1232	ND
	110P	PCB-1248	ND
	111P	PCB-1260	ND
	112P	PCB-1016	ND
	113P	toxaphene	ND

ND = Not detected

TABLE 26. ANALYSIS RESULTS -- PERCENT ETHANOL BY GAS CHROMATOGRAPHY[a]

Sample type	Site A	Site B
Distillation feed	6.9	3.9
Beer bottoms	0.9	2.4
Washout water	1.2	1.1
Byproduct	0.08[b]	0.08[b]
Cooker mash runoff	Less than 0.5	--
Product	87.0 (88.6)[c]	71.0 (73.6)[c]

[a] Accuracy estimated at ±10 percent
[b] Percent by weight
[c] Numbers in parentheses are results from hydrometer tests

deoxygenation is the presence of substances collectively called oxygen-demanding wastes (i.e., BOD_5 and COD). These substances are easily broken down or decayed by bacterial activity in the presence of oxygen; thus the presence of such materials quickly leads to a depletion of dissolved oxygen.

The disappearance of plant and animal life in waterways is an obvious result of oxygen depletion in the water. A less obvious, but important, result is a shift in water conditions from those favoring aerobic activity to those that support anaerobic activity. This occurs when the oxygen level becomes so low that the aerobic microorganisms are destroyed or driven away and anaerobic ones take their place. Products of decomposition from the different pathways are quite different. Those resulting from anaerobic conditions have unpleasant odors and are often toxic.

The discharge of the materials high in free and bound nutrients (i.e., nitrogen and phosporous) stimulate biological activity. All process streams exhibit this characterization. Nutrients are an important limiting factor in the growth of all plants. With all other factors being equal, the rate and profuseness of plant growth is proportional to the amount of nutrient available. A high concentration of nutrients will produce rapid plant growth first becoming apparent as algae bloom. The term "bloom" is used when the concentration of individual species exceeds 500 individuals per milliliter of water.

The algae blooms and large amounts of other aquatic weeds create numerous problems. Extensive plant growth is often unsightly and interferes with recreational use of water. Blooms also contribute unpleasant tastes and odors to water and become consumers of dissolved oxygen upon dying and decaying. This latter process leads to deoxygenation effects as previously discussed. However, the high nitrogen and phosphorus content of the washout waters and the beer bottom may be useful as fertilizers if applied directly to cropland.

The pH throughout the system (liquid and solid stream) was necessarily on the low side to facilitate the enzymes and yeast in the fermentation (pH range 3.4 to 4.0) process. Because of the presence in solution of carbonate and bicarbonate ions, natural waters often operate as a buffered system which makes it possible for small amounts of acid to be dissolved in the water without causing appreciable changes in the pH. However, large influxes of strong acid in limited water volumes are able to overwhelm this buffering ability of the water and cause drastic drops in pH value. The effects of these changes depend on the magnitude of the pH drop but might include aquatic life destruction, corrosion of metallic systems, and agricultural crop damage. With regard to crop damage, acidity of irrigation waters are usually of little consequence over a pH range of 4.5 to 9 since the soil is also a buffered system. It should be noted that the pH of the waste streams occurring from the alcohol production were below 4.5 and, therefore, may be toxic to plants.

The results from the metals analyses indicate that the corrosivity (low pH) problem might be significant (see Tables 15 and 21). Metals detected at significant levels (Ca, Cu, Fe, Mg, Mn and Zn) tended to increase in concentration through the system; however, the metals did tend to concentrate in the byproduct even though the pH of the byproduct and liquid streams were similar. The sources of metals throughout the process included the valves and general piping, squeezer trough, distillation columns, and holding and settling tanks. The low pH of the process streams may be actively or passively leaching metals from equipment, the majority of which were not stainless steel. The increasing levels of copper, iron, manganese, and zinc through the process are indicative of this problem.

Only traces of a few priority pollutant organics, herbicides or chlorinated pesticides, were detected in any of the samples (see Tables 16 to 19 and 22 to 25). Except for the pesticides and herbicides these traces of compounds seemed to be contamination problems rather than actual residues of the compounds.

The levels of materials analyzed are below the current promulgated Resource Conservation and Recovery Act standards. However, certain state water quality criteria are exceeded for several of the metals. For example, copper and zinc levels in the beer bottoms and washout water exceed the "protection of aquatic life" standard for Utah and all water use standards for Oregon. A more detailed review of other state criteria would most likely indicate other potential problem areas.

The results of the total phenols analysis are suspect. Two options exist. One is that the phenols were present in the process streams but did not show up in the GCMS analysis of the acid extracts. The other possibility is that the distillation process of the analysis (heat plus acid) generated phenolic compounds (see Recommendations).

5.3 QUALITY CONTROL

The program specific quality assurance/quality control (QA/QC) program entailed several factors. The objective of the laboratory QA/QC program was to meet client requirements for precise and accurate results. A few of the features of the laboratory QA/QC procedures are summarized below.

Upon receipt at the laboratory, samples were assigned laboratory identification numbers and logged in. An analysis request form was filled out by the sample control center with the aid of the project chemist. Samples were then placed in the laboratory storage cold room and analysis request forms turned over to the appropriate laboratory supervisors; thus, the samples and required analyses were clearly specified.

The laboratory analysis portion of the QA/QC program entailed several phases, from glassware preparation to reporting of results, controlled by formalized procedures. Alteration of procedures was reviewed with the project chemist.

The analytical quality procedures entailed blank, duplicate, and spike analyses. Reference samples and calibration standards were of primary standard grade, NBS traceable or of certified purity. Specific results for duplicate and spike results are detailed in Appendix A. Blank and reference sample analysis results are available, but not included in the appendix.

To assure the integrity of the reported results, the project chemist reviewed data with the analysts and discussed the results. Reported values were transcribed directly from the laboratory books to the handwritten laboratory draft. The typed Draft for Review was then checked against the original laboratory draft.

By using these specific procedures and several other integral parts of the laboratory QA/QC program, the quality of the analytical work was documented and assured.

5.4 GASEOUS RESULTS

5.4.1 Vent Samples

The vent gases from the cooker/fermentation tank were continuously sampled at both sites. Figures 18 and 19 are graphical presentations of the carbon dioxide, oxygen, total gas flow and total hydrocarbon measurements versus time for the vent sampling at Site A. Figures 20 and 21 are for the Site B sampling.

Figures 18 and 20 show, during both batches sampled, that after the preparation of the cooker mash and cook cycle the oxygen content of the tank decreased rapidly. The carbon dioxide given off by the fermenting mash quickly displaced the gases above the mash and approached 100 percent carbon dioxide. During the mash cooling cycle at Site A, the oxygen content of the ferment tank increased to about 18 percent and the carbon dioxide content decreased to about 5 percent due to the mixing. After the cooling cycle was complete, the ferment tank head gas content returned to virtually zero oxygen and almost 100 percent carbon dioxide. At Site B no cooling was necessary.

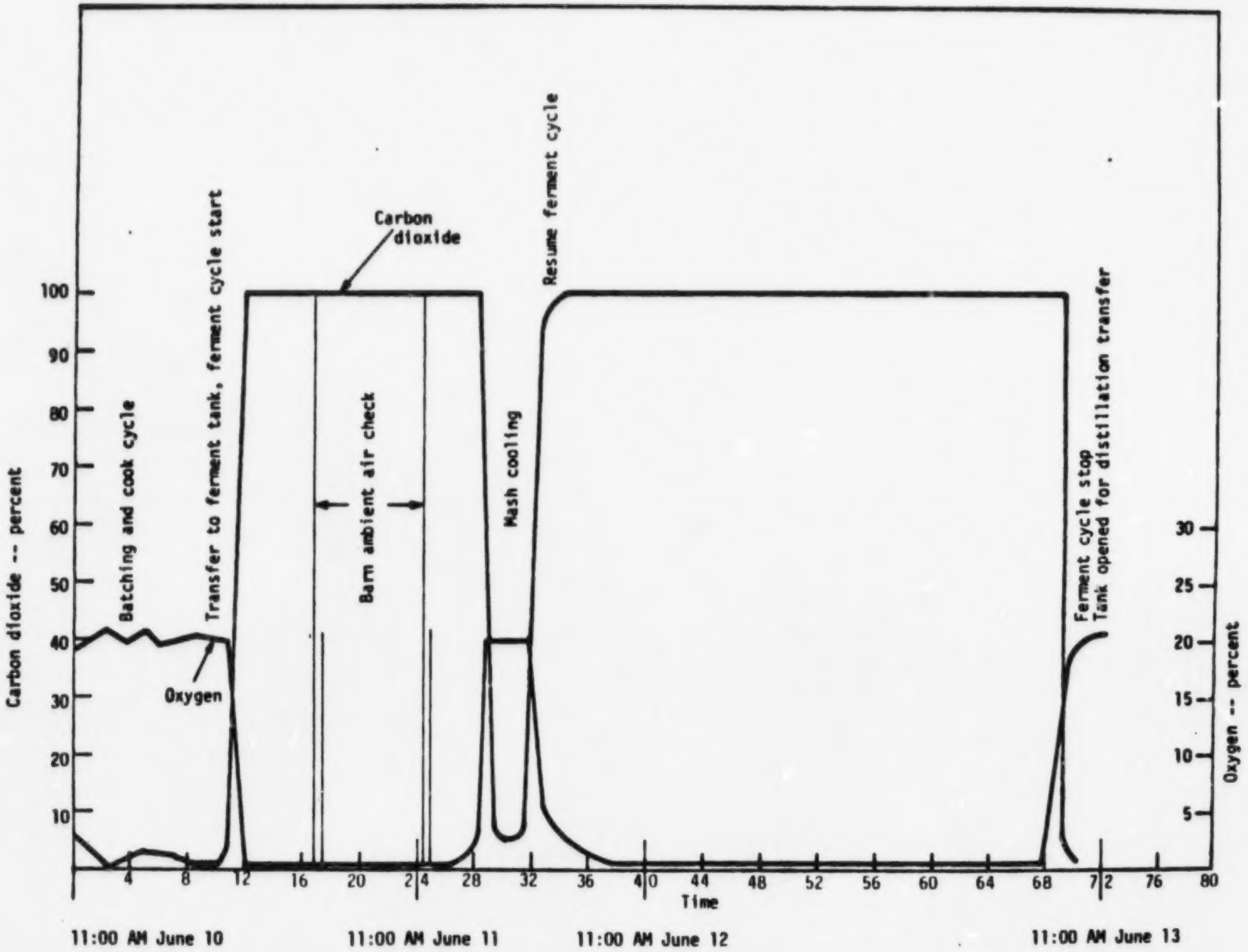

Figure 18. Site A carbon dioxide and oxygen versus hours into batch.

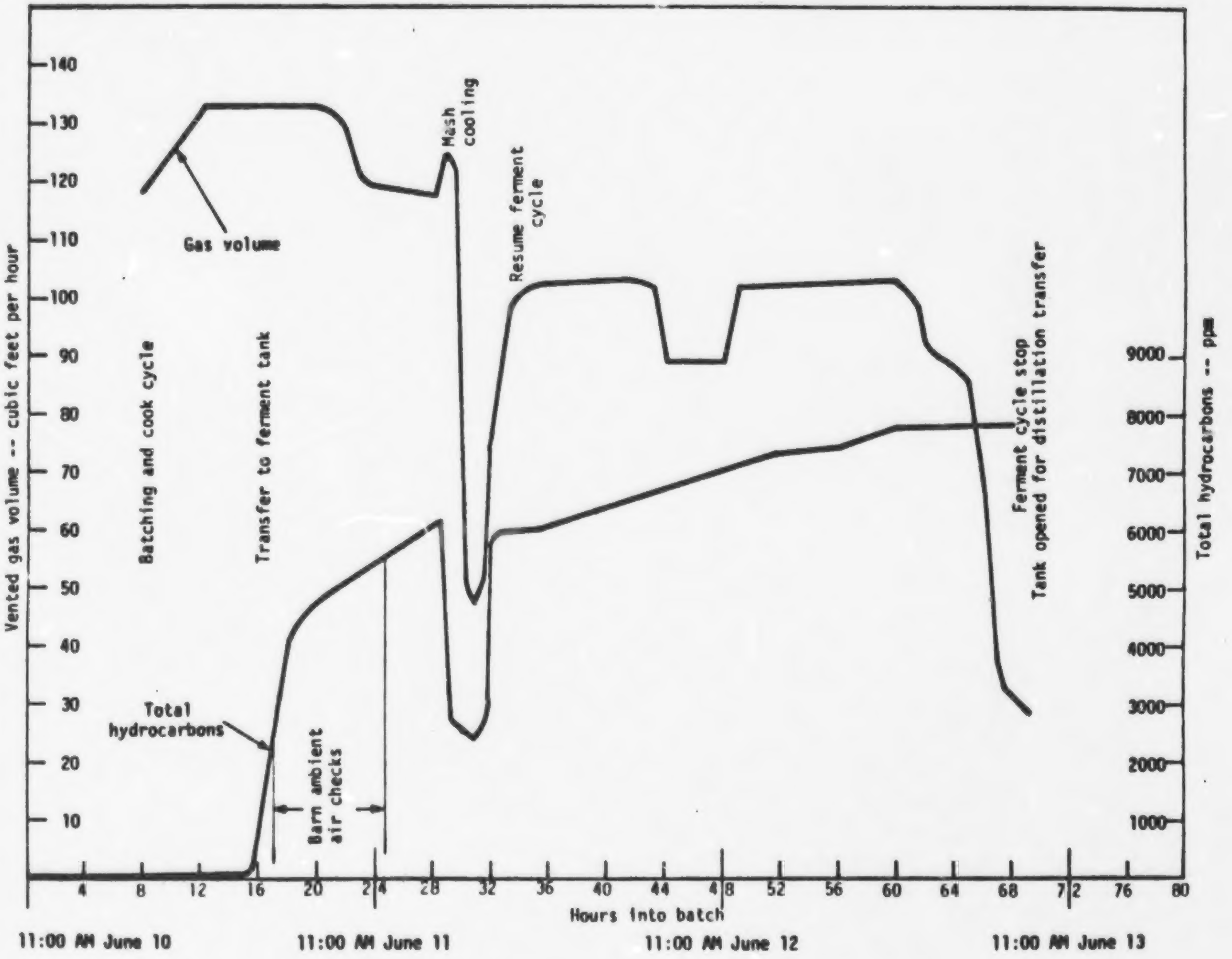

Figure 19. Site A vented gas volume and total hydrocarbons versus hours into batch.

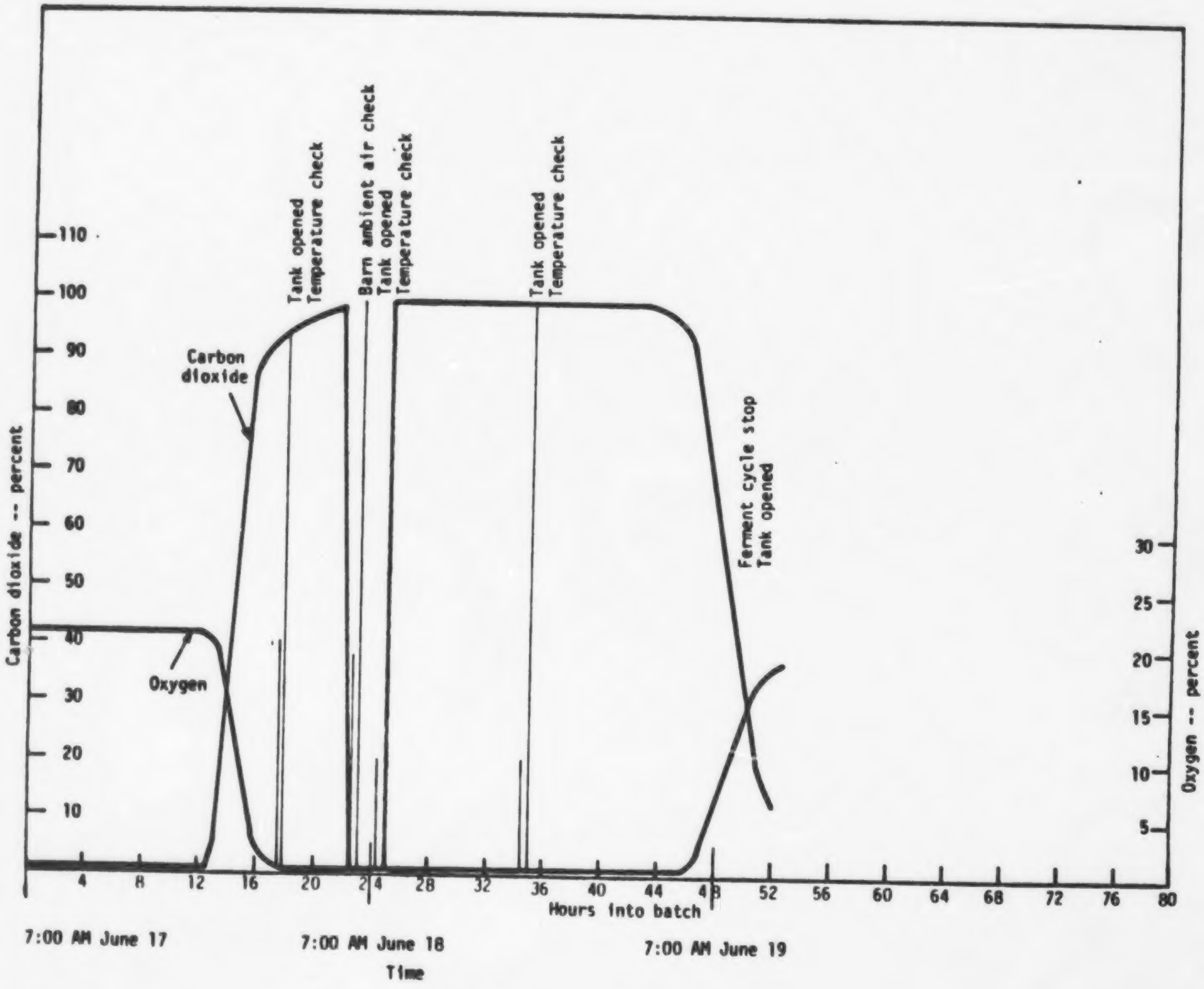

Figure 20. Site B carbon dioxide and oxygen versus hours into batch.

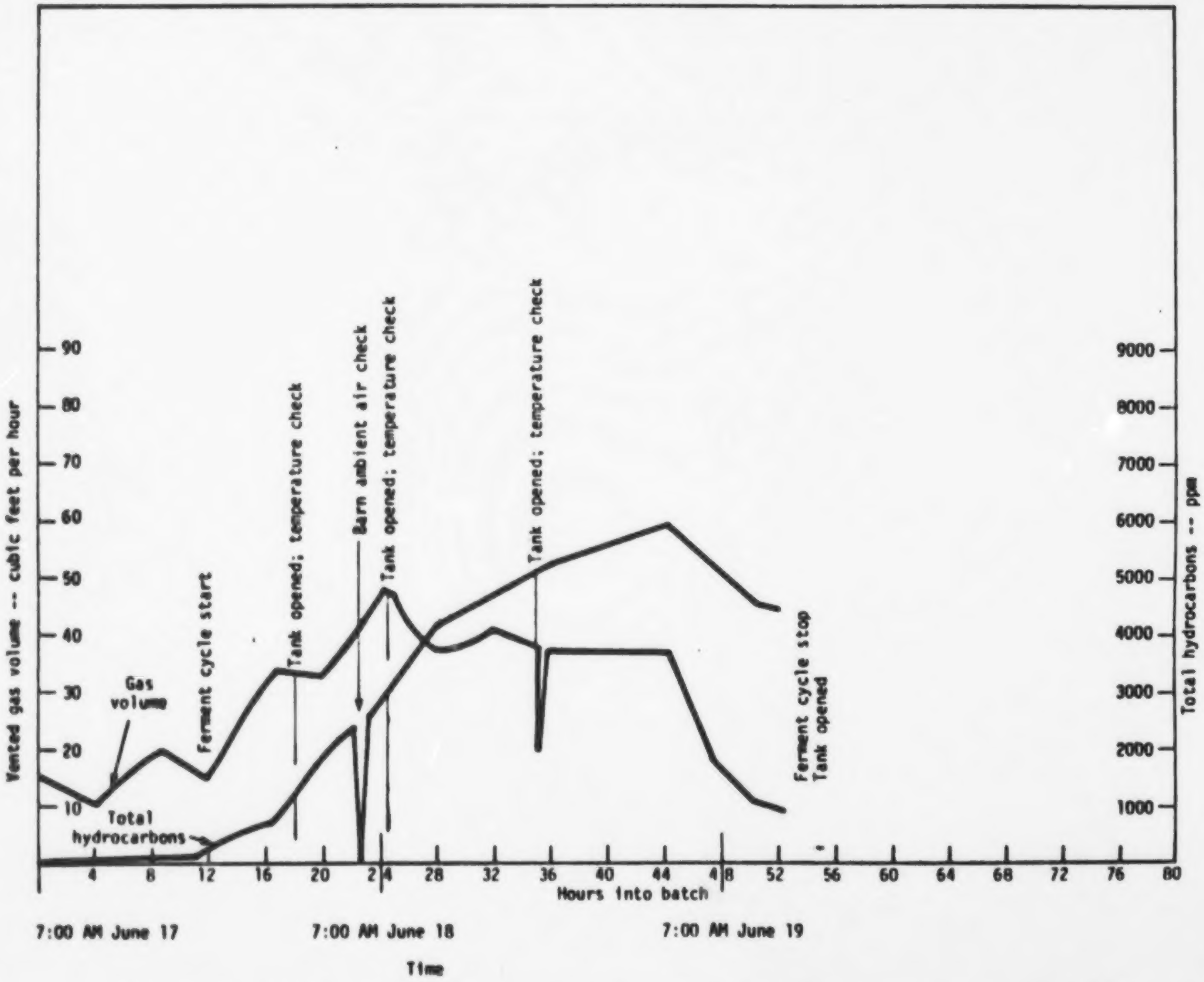

Figure 21. Site B vented gas volume and total hydrocarbons versus hours into batch.

Figures 19 and 21 show, at both Sites A and B, that after the cook cycle, the hydrocarbon content of the vented gas steadily increased throughout the ferment cycle. The vented gas volume appears to increase rapidly during the early stages of fermentation but then decreased and leveled off after about 12 to 16 hours.

As discussed in Section 3.1, gas chromatograph samples of the vented emissions were taken during the processes. Virtually all of the hydrocarbons emitted were ethanol vapors. None of the alcohols or aldehydes listed in Table 3 were found in the field tests to be present in any significant quantity. Three other hydrocarbons species were found in very small amounts typically 0.2 to 1.0 weight percent of the ethanol emitted. These three hydrocarbons could not be positively identified as any of the 21 alcohols and aldehydes for which standards were available in the field. Examination of the record indicated that these hydrocarbons were probably four to five carbon character.

In order to provide some evidence as to the identity of these trace compounds, the distillation feed samples were analyzed in the laboratory using GCMS. The results are shown in Table 27. Since this analysis is of a liquid phase sample and since all of the compounds other than methanol have lower vapor pressures than ethanol, the gas phase composition relative to ethanol would be less than shown in Table 27. Also, the analysis indicates a significant quantity of glycerol resulting from incomplete breakdown of sugar to alcohol.

TABLE 27. ANALYSIS RESULTS FOR ALCOHOLS AND ALDEHYDES IN THE DISTILLATION FEED

	Percent by weight	
Parameter	Site A	Site B
Methanol	0.02	0.01
Ethanol	6.7	3.6
1-propanol	0.01	<0.01
2-propanol	0.01	0.01
2-butanol	0.02	0.02
Pentanols	0.10	0.06
Glycol	0.05	0.03
Glycerol	1.0	0.6
Phenyl ethanol	~0.01	~0.01
Aldehydes C_1-C_5	<0.1	<0.1

5.4.2 Ambient Samples

Ambient air samples were taken around the fermentation tanks at both Sites A and B. The results showed no appreciable concentration of carbon dioxide or hydrocarbons in the air. These results were as expected since the ferment tank at Site A was vented to the outside and the doors on the building were usually open. The barn doors at Site B were open throughout the process cycle so no concentrations of carbon dioxide or hydrocarbons were found there, even though the tank was not vented outside the barn. At both sites the product tanks were open in the buildings. Since the majority of alcohol production is expected to take place during the winter when doors are closed, it would be advisable to vent fermentation tank and product tank emissions to the outdoors.

5.5 CONCLUSIONS AND RECOMMENDATIONS

The overall results indicate several areas of concern regarding the environmental impacts of solid and liquid effluents and air emissions from on-farm alcohol production. Although primary concern should be with those normal discharges from the process, one must additionally be concerned with the "dumping" of poor batches and the disposal of the solid materials other than by byproduct use, i.e., as a feedstock. For the process liquid and solid streams, these concerns include:

- High oxygen demand
- High nutrient content
- Metals in the process streams and wastes
- Low pH (acidity)

A fifth area of concern would be herbicide and/or pesticide residues from the feed grain, but this would be highly dependent upon the feedgrain supplier and the area of use. From the viewpoint of air emission, the only apparent concerns are with the venting of the fermenter off-gas and the product tank emissions to the outdoors, particularly during winter months.

The high oxygen demand and nutrient composition of the primary waste stream, i.e., the beer bottoms, could possibly be mitigated by using aerobic-anaerobic ponding. In such a treatment process a medium depth pond is used to contain the effluent for a time necessary to reduce the oxygen demand to acceptable levels. In these ponds aerobic digestion is maintained near the surface by the dissolution of ambient oxygen. At the lower depths the primary route of decomposition of organic wastes is carried out by anaerobic bacteria. Because many of the liquid and gaseous anaerobic decomposition products carried to the surface by mixing currents are utilized by the aerobic organisms, the maintenance of the aerobic zone at the surface serves to minimize the odor and toxicity problems.

Higher organic loads can be accommodated in such ponds by using a surface aerator; however, the organic load must not exceed the amount of oxygen that can be supplied by the aerator without completely mixing the pond contents or the benefits to be derived from anaerobic decomposition will be lost. Since the oxygen demand of the effluent streams from the on-farm production facilities are so high, both surface aerators and dilution may be required to obtain the desired oxygen demand reduction. The effectiveness of the aerated pond approach is dependent upon many properties of the effluent stream. Therefore, a detailed treatability study should be carried out on typical effluents to determine the appropriate design criteria and the effectiveness of this approach.

The low pH of the liquid stream potentially has two effects:

- The adverse affect on crops if used in land farming
- The corrosiveness with regard to the process equipment

Thus it is clear that these streams should be neutralized to a pH of 6 to 8 as early as possible to minimize these adverse effects. Since the acidic level is required for the fermentation process, it would appear an ideal place to neutralize would be in the holding tanks downstream of the fermentation tank. The chemical (a buffer salt) used for neutralization at this point must be benign with respect to the byproduct use.

In conclusion, the following recommendations are made:

- A treatability study be made of all effluents to determine the appropriate design criteria for waste treatment. This study should include all normal process streams as well as those from an off-spec run which might be dumped in its entirety
- The determination of appropriate neutralization chemicals for reduction of the acidic/corrosive problem
- Proper venting of all gas streams, in particular, the fermenter off-gas and the product tank vents
- A more detailed assessment of the source and fate of the metals in the system, particularly copper
- Total acidity and/or total corrosivity measurements, e.g., Langlier's Index might be useful in better understanding the internal chemistry of the system
- Further organic analysis for herbicides and pesticides in grain crops based upon a literature search to identify those elements in common use in the area of interest
- Further laboratory analysis to provide resolution of the problem of the presence of phenolic compounds

Although not previously discussed, two other areas of concern are apparent and should be addressed in future studies.

- Bioassay of all process/effluent streams to assess biological toxicity, e.g., copper toxicity to aquatic life
- Degradation (putrefaction) of byproduct if not used or properly disposed of promptly

REFERENCES

1. "Standard Methods for the Examination of Water and Wastewater," 14th Edition, 1975. APHA, AWWA, WPCF, Washington, D.C.

2. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, March 1979.

3. "Standard Operating Conditions Manual," Perkin-Elmer Corporation, Norwalk, Connecticut, September 1976.

4. "Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations," U.S. Environmental Protection Agency, FR 44, 69464, December 3, 1979.

5. "Pesticide Analytical Manual, Volume 1. Methods Which Detect Multiple Residues," Section 211.13, Food and Drug Administration, Washington, D.C.

6. "Standard Methods for the Examination of Water and Wastewater," 14th Edition, APHA, AWWA, WPCF, Method 509B, Washington, D.C., 1975.

APPENDIX A

QUALITY ASSURANCE/QUALITY CONTROL RESULTS

TABLE A-1. PRECISION ANALYSIS FOR GENERAL CHEMISTRY RESULTS -- DUPLICATE ANALYSIS

Parameter	Sample	Results	X̄	2S	2S as rel %
BOD	Fermenter mash Site A	120,000 132,000 129,000	127,000	12,500	9.8
	Beer bottoms Site B	50,000 51,000 49,500	50,000	1,500	3.1
	Washout water Site B	19,500 17,500	18,500	2,830	15
COD	Fermenter mash Site B	104,000 117,000 93,800	105,000	23,000	22
	Make-up water Site B	<5 <5	<5	--	--
TSS (All samples analyzed in duplicate; these represent worst results)	Washout water Site B	6,400 10,400 7,900 9,100	8,450	3,410	40
	Fermenter mash Site B	11,000 12,000	11,500	1,400	12
TS	Make-up water Site B	354 340 340	345	16	4.7
	Solid waste Site A	33.0 32.7	32.9	0.42	1.3

X̄ = mean value

S = standard deviation

Continued

TABLE A-1. Continued

Parameter	Sample	Results	$\bar{X}$	2S	2S as rel %
NH_3	Make-up water Site A	0.06 0.08	0.07	0.028	40[a]
	Beer bottoms (redistilled) Site A	27.4 28.9	28.1	2.1	7.5
TKN	Make-up water Site B	<0.1 <0.1	--	--	--
	Washout water Site B	419 323	371	136	37
	Beer bottoms Site A	1400 1300	1350	141	10.5
	Beer bottoms (redistilled) Site A	430 390	410	56.5	14
	Fermenter mash Site B	980 100	990	28	2.9
$SO_4^{=}$	Washout water Site B	78 74	76	5.7	7.4
	Make-up water Site A	95 90	92.5	7.1	7.6

Continued

[a] Detection limit is 0.05 mg/L

X = mean value

S = standard deviation

TABLE A-1. Continued

Parameter	Sample	Results	$\overline{X}$	2S	2S as rel %
P, Total Phosphorous	Solid waste Site B	910 875 845	877	65	7.4
	Fermenter mash Site B	379 384	381.5	7.1	1.9
NO_3's	Fermenter mash Site B	3.4 3.4	3.4	0	0
Al	Washout water Site A	1.0 1.0	1.0	0	0
	Washout water Site B	1.3 1.3	1.3	0	0
Sb	Washout water Site A	<0.02 <0.02	--	--	--
	Washout water Site B	<0.02 <0.02	--	--	--
As	Washout water Site A	<0.02 <0.02	--	--	--
	Washout water Site B	<0.02 <0.02	--	--	--

Continued

$\overline{X}$ = mean value
S = standard deviation

TABLE A-1. Continued

Parameter	Sample	Results	$\bar{X}$	2S	2S as rel %
Ba	Washout water Site A	<0.5 <0.5	--	--	--
	Washout water Site B	<0.5 <0.5	--	--	--
Be	Washout water Site A	<0.02 <0.02	--	--	--
	Washout water Site B	<0.02 <0.02	--	--	--
Bi	Washout water Site A	<0.1 <0.1	--	--	--
	Washout water Site B	<0.1 <0.1	--	--	--
Cd	Washout water Site A	3.4 ppb 3.0 ppb	3.2	0.57	18[a]
	Washout water Site B	1.4 ppb 2.2 ppb	1.8	1.1	63[a]
Ca	Washout water Site A	135 138	136.5	4.2	3
	Washout water Site B	119 121	120	2.8	2.4

Continued

[a] Detection limit is 1 ppb

X = mean value

S = standard deviation

TABLE A-1. Continued

Parameter	Sample	Results	$\overline{X}$	2S	2S as rel %
Cr	Washout water Site A	<0.05 <0.05	--	--	--
	Washout water Site B	<0.05 <0.05	--	--	--
Fe	Washout water Site A	34.2 34.7	34.5	0.71	2.0
	Washout water Site B	38.2 40.9	39.6	3.8	9.6
Pb	Washout water Site A	Contamination problems prevented accurate assessment of analytical work			
	Washout water Site B	Contamination problems prevented accurate assessment of analytical work			
Mg	Washout water Site A	84, 84, 86	84.7	2.3	2.7
	Washout water Site B	56.5 55.5	56.0	1.41	2.5
Mn	Washout water Site A	1.5 1.5	1.5	--	--
	Washout water Site B	0.75 0.78	0.765	0.042	5.5

Continued

$\overline{X}$ = mean value
S = standard deviation

TABLE A-1. Continued

Parameter	Sample	Results	$\overline{X}$	2S	2S as rel %
Ni	Washout water Site A	<0.1 <0.1	--	--	--
	Washout water Site B	<0.1 <0.1	--	--	--
Se	Washout water Site A	<0.02 <0.02	--	--	--
	Washout water Site B	<0.02 <0.02	--	--	--
Ag	Washout water Site A	<0.001 <0.001	--	--	--
	Washout water Site B	<0.001 <0.001	--	--	--
Tl	Washout water Site A	<0.02 <0.02	--	--	--
	Washout water Site B	<0.02 <0.02	--	--	--
Ti	Washout water Site A	0.045 0.040	0.0425	0.007	17
	Washout water Site B	0.02 0.04	0.03	0.028	94[a]

Continued

[a] Detection limit is 0.01 mg/L

X = mean value

S = standard deviation

TABLE A-1. Concluded

Parameter	Sample	Results	$\bar{X}$	2S	2S as rel %
Zn	Washout water Site A	1.81 1.77	1.79	0.057	3.2
	Washout water Site B	3.2 3.4	3.3	0.28	8.6
CN	Washout water Site B	<0.01 <0.01	--	--	--
Phenol	Washout water Site A	0.053 0.072	0.0625	0.027	43

TABLE A-2. ACCURACY ANALYSIS FOR GENERAL CHEMISTRY RESULTS -- SPIKED SAMPLES

Parameter	Sample	Sample concentration found mg/L	Spiked level mg/L	Percent recovery
COD	Fermenter ash Site B	105,000	500	93
NH_3	Beer bottoms (redistilled) Site A	19	10	83
	Beer bottoms Site B	13	10	89
TKN	Washout water	370	10	92
SO_4	Make-up water Site A	55	20	115
	Washout water Site B	76	20	98
P total Phosphorous	Make-up water Site A	0.1	0.25	89
	Beer bottoms Site B	240	0.25	103
NO_3	Make-up water Site A	<0.02	0.20	80
	Fermenter mash Site B	3.4	0.20	72
	Soil control Site B	0.008% by weight	0.20	92

Continued

TABLE A-2. Continued

Parameter	Sample	Sample concentration found mg/L	Spiked level mg/L	Percent recovery
Al	Fermenter mash Site B	1.3	20	120
	Solid waste Site B	<10.0 mg/kg	200 mg/kg	110
Sb	Make-up water Site B	<0.02	0.05	104
	Solid waste Site B	<0.2 mg/kg	2 mg/kg	78
As	Fermenter mash Site B	<0.02	0.20	76
	Solid waste Site B	<0.2 mg/kg	2 mg/kg	98
Ba	Fermenter mash Site B	<0.5	0.20	107
	Solid waste Site B	<5.0 mg/kg	2.0 mg/kg	104
Be	Fermenter mash Site B	<0.02	0.200	89
	Solid waste Site B	<0.2 mg/kg	2 mg/kg	86

Continued

TABLE A-2. Continued

Parameter	Sample	Sample concentration found mg/L	Spiked level mg/L	Percent recovery
Bi	Fermenter mash Site B	<0.10	0.200	57
	Solid waste Site B	<0.1 mg/kg	2 mg/kg	48
Cd	Fermenter mash Site B	0.004	0.200	88
	Solid waste Site B	<0.02 mg/kg	2 mg/kg	53
Ca	Fermenter mash Site B	150	20	98
	Solid waste Site B	230	200 mg/kg	89
Cr	Fermenter mash Site B	<0.05	0.20	88
	Solid waste Site B	<0.5 mg/kg	2.0 mg/kg	80
Fe	Fermenter mash Site B	64	20	95
	Solid waste Site B	128	200	105

Continued

TABLE A-2. Continued

Parameter	Sample	Sample concentration found mg/L	Spiked level mg/L	Percent recovery
Pb	Fermenter mash Site B	Contamination problems prevented accurate assessment of analytical work		
	Solid waste Site B	Contamination problems prevented accurate assessment of analytical work		
Mg	Fermenter mash Site B	210	20	99
	Solid waste Site B	210	200	93
Mn	Fermenter mash Site B	1.5	20	120
	Solid waste Site B	3.9 mg/kg	200 mg/kg	102
Hg	Beer bottoms Site B	<0.001	0.004	50
	Washout water Site B	<0.001	0.004	50
	Make-up water Site A	<0.001	0.004	90
	Solid waste Site B	<0.02 mg/kg	0.04 mg/kg	50

Continued

TABLE A-2. Continued

Parameter	Sample	Sample concentration found mg/L	Spiked level mg/L	Percent recovery
Ni	Fermenter mash Site B	<0.1	20	98
	Solid waste Site B	<1.0 mg/kg	200 mg/kg	92
Se	Fermenter mash Site B	<0.02	0.20	100
	Solid waste Site B	<0.2 mg/kg	2 mg/kg	97
Ag	Fermenter mash Site B	<0.001	0.20	86
	Solid waste Site B	<0.02 mg/kg	2 mg/kg	20
Tl	Fermenter mash Site B	<0.02	0.20	57
	Solid waste Site B	<0.2 mg/kg	2 mg/kg	55
Ti	Fermenter mash Site B	<0.04	0.20	75
	Solid waste Site B	<0.4 mg/kg	2 mg/kg	74

Continued

TABLE A-2. Concluded

Parameter	Sample	Sample concentration found mg/L	Spiked level mg/L	Percent recovery
Zn	Fermenter mash Site B	3.9	20	92
	Solid waste Site B	16.7 mg/kg	200 mg/kg	87
CN	Make-up water Site A	<0.005	0.020	97
Phenol	Washout water Site B	<0.05	0.050	118

TABLE A-3. RECOVERY EXPERIMENT -- ACID AND BASE/NEUTRAL COMPOUNDS
SITE B -- BEER BOTTOMS (SPIKE LEVEL = 500 μg/L)

	Acid compounds	% Recovery
21A	2,4,6-trichlorophenol	--
22A	p-chloro-m-cresol	--
24A	2-chlorophenol	--
31A	2,4-dichlorophenol	66
34A	2,4-dimethylphenol	3
57A	2-nitrophenol	--
58A	4-nitrophenol	--
59A	2,4-dinitrophenol	--
60A	4,6-dinitro-o-cresol	--
64A	pentachlorophenol	72
65A	phenol	66

	Base/Neutral compounds	% Recovery
1B	acenaphthene	--
5B	benzidine	--
8B	1,2,4-trichlorobenzene	--
9B	Hexachlorobenzene	--
12B	Hexachloroethane	--
18B	bis(2-chloroethyl)ether	--
20B	2-chloronaphthalene	--
25B	1,2-dichlorobenzene	50
26B	1,3-dichlorobenzene	--
27B	1,4-dichlorobenzene	--
28B	3,3'-dichlorobenzidine	--
35B	2,4-dinitrotoluene	--
36B	2,6-dinitrotoluene	--
37B	1,2-diphenylhydrazine (as azobenzene)	--
39B	fluoranthene	--
40B	4-chlorophenyl phenylether	--
41B	4-bromophenyl phenyl ether	--
42B	bis(2-chloroisopropyl)ether	--
43B	bis(2-chloroethoxy)methane	--
52B	hexachlorobutadiene	--
53B	hexachlorocyclopentadiene	--
54B	isophorone	--
55B	naphthalene	--
56B	nitrobenzene	52
61B	N-nitrosodimethylamine	--

Continued

TABLE A-3. Concluded

	Base/Neutral compounds	% Recovery
62B	N-nitrosodiphenylamine	--
63B	N-nitrosodi-n-propylamine	--
66B	bis(2-ethylhexyl) phthalate	12
68B	di-n-butyl phthalate	22
69B	di-n-octyl phthalate	--
70B	diethyl phthalate	--
71B	dimethyl phthalate	--
72B	benzo(a)anthracene	--
73B	benzo(a)pyrene	--
74B	3,4-benzofluoranthene	--
75B	Benzo(k)fluoranthene	--
76B	crysene	--
77B	acenaphthylene	--
78B	anthracene	--
79B	benzo(ghi)perylene	--
80B	fluorene	--
81B	phenanthrene	--
82B	dibenzo(a,h)anthracene	--
83B	indeno(1,2,3-cd)pyrene	--
84B	pyrene	--

TABLE A-4a. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE A -- MAKE-UP WATER

Compound	Fraction	Conc. (μg/L)	(Surrogates only) Spike added (μg/L)	(Surrogates only) % Recovery
d_6-Benzene	VOA	19	20	95
m-Difluorobenzene	VOA	18	20	91
d_8-Toluene	VOA	18	20	90
d_5-Phenol[a]	ACID	3	100	3
d_5-Nitrobenzene	B/N	81	100	81
1-Fluoronaphthalene	B/N	80	100	80

[a] Poor recovery possibly due to presence of Ca^{++} and Mg^{++}.

TABLE A-4b. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE A -- FERMENTER MASH

Compound	Fraction	Conc. (μg/L)	(Surrogates only) Spike added (μg/L)	(Surrogates only) % Recovery
d_6-Benzene	VOA	2	100	2
m-Difluorobenzene	VOA	45	100	45
d_8-Toluene	VOA	81	100	81
d_5-Phenol[a]	ACID	55	210	26
d_5-Nitrobenzene	B/N	85	210	40
1-Fluoronaphthalene	B/N	19	210	9

[a] Excess ethanol caused anomalous results.

TABLE A-4c. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE A -- BEER BOTTOMS

			(Surrogates only)	
Compound	Fraction	Conc. (μg/L)	Spike added (μg/L)	% Recovery
d_6-Benzene	VOA	108	100	108
m-Difluorobenzene	VOA	101	100	101
d_8-Toluene	VOA	97	100	97
d_5-Phenol	ACID	69	100	69
d_5-Nitrobenzene	B/N	52	100	52
1-Fluoronaphthalene	B/N	12	100	12

TABLE A-4d. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE A -- WASHOUT WATER

			(Surrogates only)	
Compound	Fraction	Conc. (μg/L)	Spike added (μg/L)	% Recovery
d_6-Benzene	VOA	19	20	94
m-Difluorobenzene	VOA	18	20	89
d_8-Toluene	VOA	18	20	88
d_5-Phenol[a]	ACID	62	100	62
d_5-Nitrobenzene	B/N	1	100	1
1-Fluoronaphthalene	B/N	11	100	11

TABLE A-4e. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE A -- SOLID WASTE

Compound	Fraction	Conc. (μg/L)	(Surrogates only) Spike added (μg/L)	(Surrogates only) % Recovery
d_6-Benzene	VOA			
m-Difluorobenzene	VOA			
d_8-Toluene	VOA			
d_5-Phenol	ACID	1360	2000	68
d_5-Nitrobenzene	B/N	1740	2000	87
1-Fluoronaphthalene	B/N	840	2000	42

TABLE A-4f. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE B -- MAKE-UP WATER

Compound	Fraction	Conc. (μg/L)	(Surrogates only) Spike added (μg/L)	(Surrogates only) % Recovery
d_6-Benzene	VOA	20	20	100
m-Difluorobenzene	VOA	19	20	96
d_8-Toluene	VOA	19	20	98
d_5-Phenol	ACID	69	100	69
d_5-Nitrobenzene	B/N	73	100	73
1-Fluoronaphthalene	B/N	75	100	75

TABLE A-4g. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE B -- FERMENTER MASH

Compound	Fraction	Conc. (μg/L)	(Surrogates only) Spike added (μg/L)	(Surrogates only) % Recovery
d_6-Benzene	VOA	127	100	127
m-Difluorobenzene	VOA	99	100	99
d_8-Toluene	VOA	87	100	87
d_5-Phenol	ACID	146	200	73
d_5-Nitrobenzene	B/N	212	200	106
1-Fluoronaphthalene	B/N	36	200	18

TABLE A-4h. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE B -- BEER BOTTOMS

Compound	Fraction	Conc. (μg/L)	(Surrogates only) Spike added (μg/L)	(Surrogates only) % Recovery
d_6-Benzene	VOA	82	100	82
m-Difluorobenzene	VOA	95	100	95
d_8-Toluene	VOA	93	100	93
d_5-Phenol	ACID	64	100	64
d_5-Nitrobenzene	B/N	75	100	75
1-Fluoronaphthalene	B/N	78	100	78

TABLE A-4i. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE B -- WASHOUT WATER

Compound	Fraction	Conc. (µg/L)	(Surrogates only) Spike added (µg/L)	(Surrogates only) % Recovery
d_6-Benzene	VOA	92	100	92
m-Difluorobenzene	VOA	88	100	88
d_8-Toluene	VOA	84	100	84
d_5-Phenol	ACID			
d_5-Nitrobenzene	B/N			
1-Fluoronaphthalene	B/N			

TABLE A-4j. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE B -- WASHOUT WATER

Compound	Fraction	Conc. (µg/L)	(Surrogates only) Spike added (µg/L)	(Surrogates only) % Recovery
d_6-Benzene	VOA	20	20	100
m-Difluorobenzene	VOA	20	20	99
d_8-Toluene	VOA	19	20	97
d_5-Phenol	ACID			
d_5-Nitrobenzene	B/N			
1-Fluoronaphthalene	B/N			

TABLE A-4k. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE B -- WASHOUT WATER

			(Surrogates only)	
Compound	Fraction	Conc. (μg/L)	Spike added (μg/L)	% Recovery
d_6-Benzene	VOA	17	20	86
m-Difluorobenzene	VOA	16	20	82
d_8-Toluene	VOA	16	20	80
d_5-Phenol	ACID	66	100	66
d_5-Nitrobenzene	B/N	5	100	5
1-Fluoronaphthalene	B/N	14	100	14

TABLE A-41. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE B -- WASHOUT WATER

			(Surrogates only)	
Compound	Fraction	Conc. (μg/L)	Spike added (μg/L)	% Recovery
d_6-Benzene	VOA	94	100	94
m-Difluorobenzene	VOA	67	100	67
d_8-Toluene	VOA	80	100	80
d_5-Phenol	ACID			
d_5-Nitrobenzene	B/N			
1-Fluoronaphthalene	B/N			

TABLE A-4m. SURROGATE SPIKE RESULTS -- ORGANICS -- SITE B -- SOLID WASTE

			(Surrogates only)	
Compound	Fraction	Conc. (µg/L)	Spike added (µg/L)	% Recovery
d_6-Benzene	VOA			
m-Difluorobenzene	VOA			
d_8-Toluene	VOA			
d_5-Phenol	ACID	1020	2000	51
d_5-Nitrobenzene	VOA	2320	2000	116
1-Fluoronaphthalene	VOA	1640	2000	82

TABLE A-5. RECOVERY EQUIPMENT -- PESTICIDES/HERBICIDES -- SITE A -- FEED GRAIN (SPIKE LEVEL = 500 μg/L)

	Pesticides	% Recovery
89P	aldrin	28
90P	dieldrin	48
91P	chlordane	--
92P	4,4'-DDT	22
93P	4,4'-DDE	30
94P	4,4'-DDD	30
95P	-endosulfan	20
96P	-endosulfan	30
97P	endosulfan sulfate	6
98P	endrin	64
99P	endrin aldehyde	--
100P	heptachlor	50
101P	heptachlor epoxide	46
102P	-BHC	140
103P	-BHC	--
104P	-BHC	90
105P	-BHC	--
106P	PCB-1242	--
107P	PCB-1254	--
108P	PCB-1221	--
109P	PCB-1232	--
110P	PCB-1248	--
111P	PCB-1260	--
112P	PCB-1016	--
113P	toxaphene	--

Herbicides	% Recovery
2,4-Dichlorophenoxyacetic Acid	150
2,4,5-Trichlorophenoxyacetic Acid	--
Silvex	--